MOLECULAR ORBITAL TREATMENTS OF THE AQUO AND AMMINE COMPLEXES OF IRON, COBALT AND NICKEL

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INTRODUCTION

Background

The majority of octahedral cobalt(II) complexes are high-spin with magnetic moments between 4.3 and 5.2 Bohr magnetons.[14] A few octahedral cobalt(II) complexes are low-spin.[30] Recently, there have been reported some octahedral cobalt(II) complexes which have magnetic moments of approximately three Bohr magnetons.[8,33] It has been proposed that these unusual magnetic moments are due to a Boltzmann distribution over the thermally accessible spin states ($^4T_1$ and ^2E) near the cross-over point from high-spin to low-spin.[8,33] This proposal provides a satisfactory semi-quantitative explanation of these low magnetic moments; however, it is desirable to have a more complete elucidation of the phenomena involved in these unusual complexes. This will, hopefully, lead to a better understanding of the cross-over point and, consequently, a better understanding of transition metal complexes.

For several decades, the molecular orbital (MO) theory, especially the linear combination of atomic orbital (LCAO) form of this theory, has been used as an aid in interpreting and assigning electronic structures and transitions of many

compounds, particularly organic compounds. The principles are equally applicable to inorganic compounds in general and to the unusual cobalt(II) complexes in particular. It is logical then to attempt to use this theory to obtain a better understanding of the phenomena involved in these unusual complexes.

Unfortunately, it is not possible (at this time) to subject the unusual complexes to a molecular orbital treatment for two reasons. They are not sufficiently characterized (that is, there is still some doubt as to their configurations and certainly the internuclear distances are not known), and the molecular orbital methods have been applied to only a few transition metal complexes (see below).

In this investigation, some approximate molecular orbital methods have been tested on several transition metal complexes which are well understood (in terms of electronic transitions), which have much higher symmetry than the unusual cobalt(II) complexes and in which the internuclear distances are known or for which very reasonable estimates may be made.

Each of the cobalt(II) complexes which has an unusual magnetic moment contains immine nitrogen donors[8,33] and, thus, it is desirable to choose compounds for treatment that contain nitrogen as a donor atom. Furthermore, if the proposal of a Boltzmann distribution is valid, then the

$[Co(H_2O)_6]^{3+}$ ion should be investigated, since this ion has been characterized as low-spin but near the cross-over point.[24] This compound also affords the opportunity to investigate the importance of pi bonding which should have considerable influence on the properties of the unusual cobalt(II) complexes.

Definition of terms

When the LCAO approximation is substituted into the Schrodinger equation and the variational theorem is applied, the Schrodinger equation reduces to a secular determinant of the form

$$|H_{ij} - G_{ij} E| = 0 \qquad (1)$$

where

$$H_{ij} = \int \phi_i H \phi_j d\tau \ , \ G_{ij} = \int \phi_i \phi_j d\tau = aS_{ij} \ , \ S_{ij} = \int \chi_i \chi_j d\tau \ ,$$

E is the eigenvalue corresponding with the molecular orbital $\Psi_i = \sum_j \phi_i c_{ij}$, $\phi_i = \sum_j \chi_i b_{ij}$, H is a sum of one electron Hamiltonian operators, Ψ_i is a molecular orbital, ϕ_i is a group orbital, χ_i is an atomic orbital, and a is a numerical constant. H_{ij} is called the coulomb integral if i=j, and the resonance integral if $i \neq j$. G_{ij} is the group overlap integral and S_{ij} is the (two center) overlap integral.

The secular determinant can frequently be partially diagonalized, by group theoretical methods,[1] into a form in which the most complicated determinant is small, thus reducing the work by a considerable amount.

Review of literature

In the past several years there have been reported several attempts to calculate one-electron molecular orbital energy levels for transition metal complexes. The procedure used is a semi-empirical one originally proposed by Mulliken[22] and first applied to a transition metal compound, the permanganate ion, by Wolfsberg and Helmholz.[37]

Ballhausen and Gray[2] modified the procedure of Wolfsberg and Helmholz for estimating the coulomb and resonance integrals and treated the vanadyl ion. Since then, the permanganate ion (treated by two different groups of investigators),[10,36] the Cr^{3+} ion in crystals,[17] VCl_4, $CuCl_4^{2-}$, $NiCl_4^{2-}$, and CuF_6^{4-},[15] TiF_6^{3-} (treated by two different groups of investigators),[5,9] VF_6^{2-} and VF_6^{3-},[4] pi bonding in sulfones[16] and the hexaamines of Cr^{3+}, Co^{2+}, Co^{3+}, and Ni^{2+},[7] have been treated using the methods of Ballhausen and Gray for estimating the resonance integrals. However, each of these investigators utilizes a different procedure for estimating the coulomb integrals.

The methods of estimating the coulomb integrals fall into two classes. One of these methods is to make an educated guess based on previous estimates and chemical intuition as to what the proper values should be. In the other method, the coulomb integral is equated to the negative of the valence state ionization potential (defined below) which is calculated by approximating the valence state as a linear combination of configurations, and using the observed spectroscopic energies of these configurations to determine the valence state ionization potential.

Ohno, Tanabe, and Sasaki[23] have used a slightly different modification of the Wolfsberg-Helmholz method of estimating the resonance integrals in their treatment of the iron-porphyrin system.

In order to test some of the approximate methods mentioned above as well as to build a foundation upon which further work on the unusual cobalt(II) complexes may be accomplished, the following complexes have been investigated: the hexaaquo complexes of iron(II), iron(III), cobalt(II), cobalt(III), and nickel(II) and the hexaamine complexes of cobalt(II), cobalt(III), and nickel(II). Metal wave functions corresponding to atomic wave functions of several different integral charges q have been used for each complex. In all cases the resonance integral has been estimated by two different methods and the eigenvectors

from each of these methods have been analyzed by two different methods of population analysis. For the aquo complexes pi bonding has in turn been included and omitted. The $[Co(H_2O)_6]^{3+}$ ion has been treated by the above procedures and in addition calculations using a slightly different method of estimating the coulomb integral for the donor atom and calculations at a different internuclear distance have been made.

The procedure followed is similar to that of Ballhausen and Gray[2] but, for the sake of clarity, the entire procedure is outlined below.

PROCEDURE

Symmetry and wave functions

The symmetry of the ammine and of the aquo complexes in which pi bonding is neglected is O_h (neglecting hydrogens). When pi bonding is included in the aquo complexes, an assumption must be made about the orientation of the hydrogen atoms. The assumption will be made that the symmetry is T_h, that is, that water molecules have their C_{2v} axes collinear with the metal-oxygen bond axis, and the hydrogen atoms of waters in trans positions lie in a molecular reflection plane. The donor pi orbitals are perpendicular to this plane. For simplicity the symmetry orbitals are classified according to the group O_h throughout.

The internuclear distances used for the compounds studied are as follows: Fe^{2+}-$O(H_2O)$ 2.17 Å as observed in $Fe_3(PO_4)_2\ 4H_2O$,[13] Fe^{3+}-$O(H_2O)$ 2.08 Å as observed in $(NH_4)_2[FeCl_5H_2O]$,[34] Co^{2+}-$O(H_2O)$ 2.08 Å as observed in $[Co(C_2H_3O_2)_2(H_2O)_4]$,[34] Co^{3+}-$O(H_2O)$ 1.98 Å (estimated), Ni^{2+}-$O(H_2O)$ 2.08 Å as observed in $[Ni(C_2H_3O_2)_2(H_2O)_4]$,[34] Co^{2+}-$N(NH_3)$ 2.10 Å (estimated), Co^{3+}-$N(NH_3)$ 2.00 Å as observed in $K[Co(NH_3)_2(NO_2)_4]$.[34]

The observed distances are from crystal x-ray data. For the other two values it was estimated that the covalent

radius of Co(II) is 0.10 Å greater than that of Co(III) in agreement with Pauling's table of octahedral radii.[25] Further, the Cr-O internuclear distance in $[Cr(H_2O)_6]^{3+}$ is 1.97 Å[12] and since Co^{3+} should have a slightly larger effective radius than Cr^{3+}, the estimate of 1.98 Å for the Co^{3+}-$O(H_2O)$ internuclear distance is reasonable.

A minimal set of atomic orbitals has been used throughout, viz. 3d, 4s, and 4p for cobalt, 2s and 2p for the donor.

The metal atomic orbitals are the double zeta functions of Richardson et al.[28,29] For the donor atoms, the double zeta functions of Clementi[6] have been used. Richardson does not give a 4p wave function for Co^{3+} or Fe^{3+}. These have been estimated by graphical extrapolation of the 4p wave functions for the neutral, singly ionized, and doubly ionized cobalt and iron wave functions of Richardson et al.[29] and then normalized to unity.*

Hybridized orbitals have been used for the donor atoms. The amount of hybridization has been estimated to be

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*The form of these wave functions is:

$$R_{4p}(Fe) = 0.10308\chi(10.60) - 0.36541\chi(4.17) + 1.05510\chi(1.80)$$

$$R_{4p}(Co) = 0.10098\chi(11.05) - 0.35555\chi(4.385) + 1.05194\chi(1.86) .$$

the same as that in the lone pair orbitals of the free water wave functions of McWeeny and Ohno[18] and the free ammonia wave function of Tsuchida and Ohno.[35] These lone pair orbitals are linear combinations of Slater type wave functions and include hydrogen 1s components as well as nitrogen or oxygen 1s components. It will be assumed that the ratio of coefficients of the 2s and 2p Slater type orbitals from these lone pair orbitals can be carried over to the present calculations and can be used with the double zeta wave functions of Clementi to form the donor hybrids. In the oxygen case it was necessary to first form linear combinations of sigma and of pi symmetry. The resulting hydrids are

$$\chi(N_\sigma) = 0.667435\chi(2s) + 0.744667\chi(2p_z)$$

$$\chi(O_\sigma) = 0.836458\chi(2s) + 0.548032\chi(2p_z)$$

where the χ's are double zeta atomic wave functions. The pi symmetry orbital is an atomic 2p orbital:

$$\chi(O_\pi) = \chi(2p_x) .$$

When calculations were made that neglected pi bonding, this pi symmetry orbital was considered to be localized on the oxygen atom, that is, non-bonding. In none of the calculations were any of the hydrogen orbitals included.

Coulomb integrals

The coulomb integrals were estimated by equating them to the negative of the valence state ionization potentials (VSIP). The valence state is defined by Moffitt[19] and extended by Ballhausen and Gray[2] as that hypothetical state of each atom in a molecular aggregate which has been separated to an infinite distance, while leaving the orbitals with the same hybridization and electronic population as was found in the molecular aggregate before the atoms were separated. The separated atoms may be assigned fractional charges.

The valence state can be written as a linear combination of all the electronic states (including the continuum) possible for an atom or ion. The present calculations utilize the minimal set of atomic orbitals; therefore we approximate the valence state by a few observed configurations which involve the minimal set of orbitals.

The valence state energy is calculated from the average energy of a configuration,[31] which is the weighted mean of the energies of the terms arising from the configuration, relative to the ground state of the atom or ion in question. The weighting factor has been taken as equal to the total degeneracy (spin and orbital) of the term, provided the J components (J is the orbital angular momentum quantum number) are not too widely separated. If the J components

are widely separated, the average is taken over the energies of the J components, weighted by their degeneracies.

For the donor atoms (either nitrogen or oxygen) the minimal set of observed configurations is comprised of $2s^2 2p^n$ and $2s2p^{n+1}$ configurations where n = 3 for nitrogen and n = 4 for oxygen. Another configuration, p^{n+2}, is possible but has been observed in only one case[20] and is of very high energy and is therefore not included. A typical plot of these data is shown in Figure 1.

The linear combination of these configurations is made so that the electron distribution on the donor atom is reproduced. The electron distribution on the donor atom is determined from a population analysis of the ligand wave functions by the Mulliken[21] method. It would have been possible to analyze them by the Smith method (see below) for comparison, but the difference in the calculated VSIPs would be small.

If pi bonding is neglected, the linear combination for the donor atom (D) is:

$$_s(2-Q)C_s^2 + R_s\ _p(2-Q)C_p^2 + R_p = a(s^2p^{n-Q}) + b(sp^{n+1-Q}) \qquad (2)$$

where a and b are the coefficients of the linear combination, Q is the charge on each donor atom, C_s and C_p are determined by $\chi(D_\sigma) = C_s\chi(2s) + C_p\chi(2p)$, R_s and R_p are the s and p

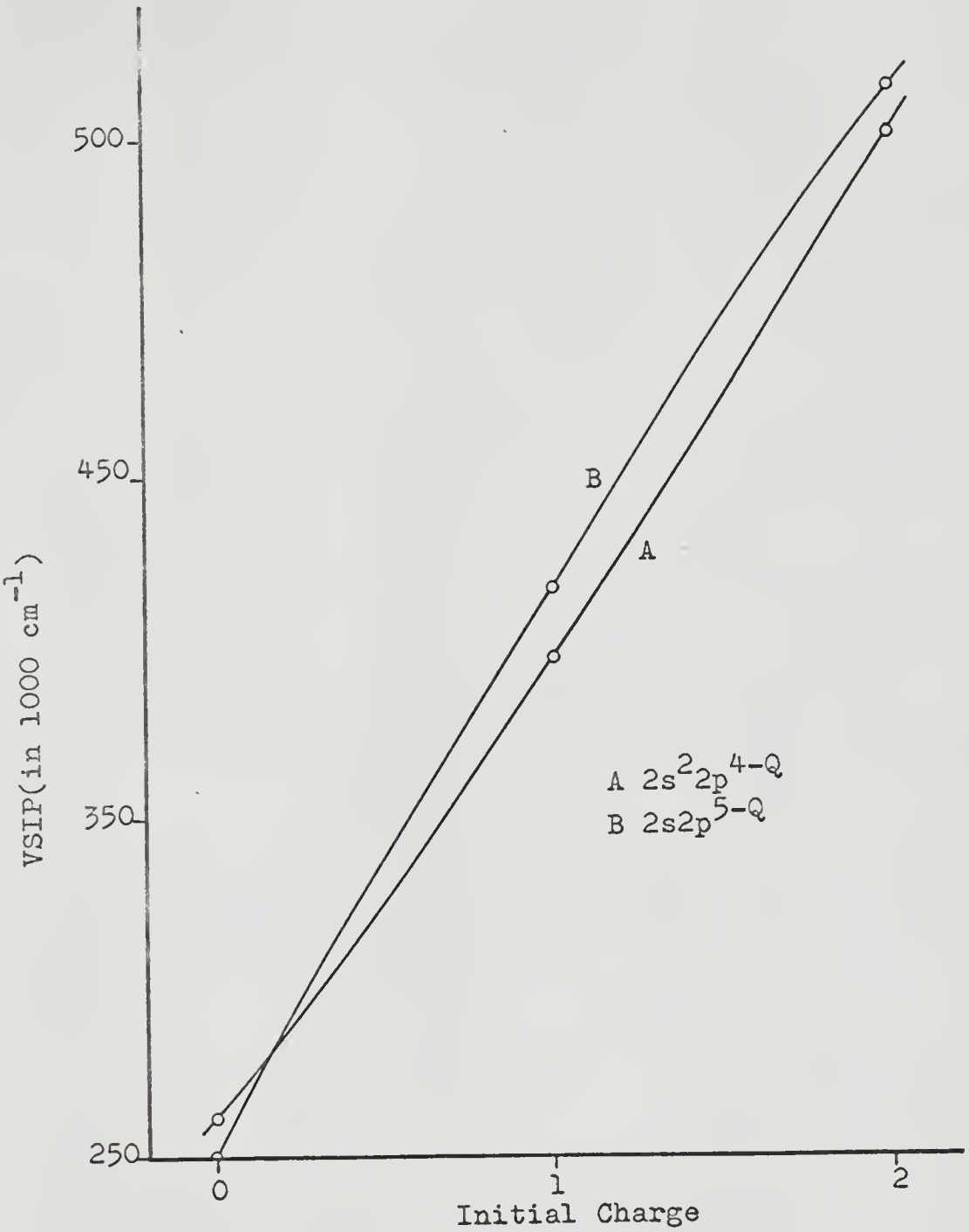

Fig. 1.-VSIP of 2s electron on oxygen.

populations respectively, in the orbitals on the donor atom which are bonded to hydrogens.

The left side of this equation is the valence state configuration of the donor atom. All positive charge (Q) on the donor is assumed to arise from the removal of electron density from the donating sigma orbital only. In the free donor molecule there are two electrons in this orbital and (2-Q) electrons when the atom is in its valence state. C_s^2 and C_p^2 are, respectively, the probabilities that an electron in this orbital is an s or a p electron. R_s and R_p are determined from the population analysis (see above) in the same manner.

The right side of eq. (2) is the linear combination of configurations which approximates the valence state. The electronic configurations in the parenthesis reflect the manner in which the configurations vary along the curves in Figure 1.

Other lines could have been drawn to connect the points in Figure 1 and in that case, other configurations would be used to form the linear combination. However, these are the best lines to use since other lines would lead to the hypothetical ionization of a fraction of an electron. This is the case in the investigations of Bedon et al.,[4,5] where the lines were extrapolated into regions of the graphs such that there was only a fraction of an s electron remaining in the configuration to be ionized.

The coefficients (a and b) are then determined by equating the s and p populations on both sides of eq. (2). The VSIP energies for the removal of an s electron from each configuration are then substituted into the equation

$$V(s) = aV_a + bV_b \qquad (3)$$

where V(s) is the valence state ionization potential of an s electron, V_a is the VSIP of an s electron in the configuration s^2p^{n-Q}, and V_b is the VSIP of an s electron in the configuration sp^{n+1-Q}. A similar relation holds for V(p).

The VSIP of an electron in the orbital D_σ is the sum of the probabilities of that electron being an s or p electron times the respective ionization potential of an s or a p electron in the valence state. Thus

$$H_D = -VSIP = -C_s^2 \quad V(s) - C_p^2 \quad V(p) \qquad (4)$$

An alternate procedure used to test the sensitivity of the self-consistent parameters to the estimate of the coulomb integral for the donor was to remove the same amount of s and p electron density from each configuration as was removed from the donating orbital. Thus eq. (2) becomes

$$s^{(2-Q)}C_s^2 + R_s \; p^{(2-Q)}C_p^2 + R_p = a(s^{2-QC_s{}^2} \; p^{n-QC_p{}^2}) + b(s^{1-QC_s{}^2} \; p^{n+1-QC_p{}^2}) \qquad (5)$$

The coefficients (a and b) are then determined as above. These coefficients were then used in equation (3) to determine the valence state ionization potential of an s

electron and in the similar equation for V(p). It is this step which makes these estimates inaccurate. However, this procedure consistently raises the coulomb integral of the donor atom by approximately 2000 cm^{-1} (0.25 eV) so that some information may be obtained from the results of this method.

Analogous procedures were used to calculate the VSIP of an electron from the pi symmetry orbital.

For the metal VSIP's the above method is not sufficient. There are at least six configurations[20] arising from the minimal set of basis orbitals which contribute to the valence state for each ion of integral charge, and there are only four conditions, the d, s, and p populations and the normalization condition. When an attempt is made to interpolate for fractional charge as was done for the donor, the number of unknowns doubles without any increase in the number of conditions.

As a substitute for this approximation, the procedure of Ballhausen and Gray[2] has been used for estimating the VSIP's. In this procedure the various configurations are arranged in groups of three for each type of electron, that is, d, s, or p. The groupings are made so that the three configurations which are most important to the energy of the state from which a d, s, or p electron is removed, are included. Curves similar to Figure 1 have been drawn so

that the charge adjustment of the configurations is made by removing electron density from the d population only. Thus, for example, the final form for the linear combination which was used for calculating the valence state ionization potential for a d electron of cobalt is

$$a(d^{9-z}) + b(d^{8-z}s) + c(d^{8-z}p) = d^{\alpha}s^{\beta}p^{\gamma} \qquad (6)$$

where a, b, and c are the coefficients of the linear combinations, Z is the charge on the cobalt, α, β, and γ are the occupation numbers of the d, s, and p orbitals, respectively.

In Appendix I are the generalized solutions for the coefficients of all the linear combinations as well as the equations that were fitted to the VSIP data of Basch and Viste.[3]

Overlap integrals

The group overlap integrals were calculated from two center overlap integrals by standard group theoretical procedures.[1] The two center atomic overlap integrals, as well as the atomic dipole moment integrals (see below) were evaluated on the IBM 709 at the University of Florida Computer Center using a program written by Corbato and Switendick.[27] In Table 1 are tabulated all of the group overlap integrals. Overlap of donor orbitals on different sites is assumed to be zero.

TABLE 1

GROUP OVERLAP INTEGRALS

Overlap of Metal Atom	Ligand Atom	Distance	Symmetry				
			a_{1g}	e_g	t_{1u}	$t_{1u}(\pi)$	t_{2g}
Fe^{1+}	O	2.17	0.68363	0.20188	0.58137	0.19405	0.06801
Fe^{2+}	O	2.17	0.68363	0.15142	0.55751	0.16358	0.04911
Fe^{3+}	O	2.17	0.68363	0.11250	0.49819	0.13531	0.03540
Fe^{1+}	O	2.08	0.72561	0.23009	0.59928	0.21305	0.08153
Fe^{2+}	O	2.08	0.72561	0.17558	0.59437	0.18529	0.05974
Fe^{3+}	O	2.08	0.72561	0.13250	0.54382	0.15661	0.04364
Co^{0+}	O	2.08	0.72471	0.26142	0.40862	0.18628	0.09489
Co^{1+}	O	2.08	0.72471	0.20030	0.60560	0.21001	0.06952
Co^{2+}	O	2.08	0.72471	0.15176	0.58522	0.17892	0.05079
Co^{1+}	O	1.98	0.77367	0.23185	0.62496	0.23339	0.08533
Co^{2+}	O	1.98	0.77367	0.17897	0.62643	0.20565	0.06333
Co^{3+}	O	1.98	0.77367	0.13739	0.57811	0.17499	0.04726
Co^{3+}	O	1.93	0.79692	0.15055	0.60360	0.18948	0.05305
Ni^{1+}	O	2.08	0.48062	0.23243	0.43098	0.19221	0.08142
Ni^{2+}	O	2.08	0.48062	0.17466	0.60825	0.20693	0.05950
Ni^{3+}	O	2.08	0.48062	0.13221	0.57218	0.17117	0.04360
Co^{1+}	N	2.10	0.83995	0.22588	0.63824	---	---
Co^{2+}	N	2.10	0.83995	0.17483	0.64674	---	---
Co^{2+}	N	2.00	0.88513	0.20056	0.67824	---	---
Co^{3+}	N	2.00	0.88513	0.15752	0.64472	---	---
Ni^{1+}	N	2.06	0.86331	0.20968	0.65132	---	---
Ni^{2+}	N	2.06	0.86331	0.16308	0.65315	---	---

Resonance integrals

The approximation of Wolfsberg and Helmholz[37] and the modification of this approximation due to Ballhausen and Gray[2] have been used to calculate the resonance integrals. The Wolfsberg and Helmholz approximation is

$$H_{ij} = FG_{ij}(H_{ii} + H_{jj})/2 \qquad (7)$$

and the Ballhausen and Gray modification is

$$H_{ij} = -FG_{ij}(H_{ii}H_{jj})^{1/2} \qquad (8)$$

where F is an empirical proportionality constant.

Ballhausen and Gray state[2] that the geometric mean is preferable since the resonance energy is expected to decrease rapidly as the difference in the coulomb energies becomes greater. However, in at least one case reported in the literature[17] in which this approximation was used, it was necessary to artifically assume a very small charge dependence for the coulomb integral in order to obtain self-consistency of the assumed and calculated charge densities. A charge dependence equal to the ground state ionization potential would have led to divergence.

Ohno, Tanabe and Sasaki[23] have also modified the approximation of Wolfsberg and Helmholz to the form

$$H_{ij} = G_{ij}\left(F\frac{H_{ii} + H_{jj}}{2} + \frac{H'_{ii} + H'_{jj}}{2}\right) \qquad (9)$$

This modification consists of separating the electrostatic

part, H'_{ii} and H'_{jj} from H_{ii} and H_{jj}. This is done in order to fulfill the requirement that the resulting orbital energy differences should not change, if the zero point of energy is changed by adding a constant potential to the Hamiltonian. For these calculations the electrostatic part is zero.

Wolfsberg and Helmholz[37] originally used an F of 1.67 for sigma orbitals and 2.00 for pi orbitals. Ballhausen and Gray[2] have used F = 2.00 for both sigma and pi orbitals. Since there is no fundamental reason for expecting that there should be different values for sigma and pi orbitals except that values near these gave satisfactory results in energy level calculations of homonuclear diatomic molecules of first and second row elements, the value of 2.00 seems reasonable and has been used throughout these calculations. It is obvious that as F is decreased, 10Dq will be decreased. Cotton and Haas[7] have varied F in their calculations and they concluded that it was necessary to use different F's for different complexes, in order to obtain agreement with the experimental 10Dq values. It seems more reasonable to adopt one value of F for all complexes, as has been done here.

Population analysis

The methods of population analysis of Mulliken[21] and of Smith[32] have been used to estimate the electron distribution in the self-consistent complexes.

In the Mulliken method the electron density of the molecule is divided into atomic contributions and the coefficient of the square of an atomic orbital is identified with the population of that orbital. Thus, the contribution of $\phi_i = \sum_k \chi_k b_{ki}$ to the total electron density arising from $\Psi_j = \sum_i \phi_i c_{ij}$ is

$$\rho_i = N(j)(\sum_i \phi_i c_{ij})^2 \qquad (10)$$

where $N(j)$ is the number of electrons in Ψ_j.

The Mulliken approximation is that the cross product term should be equally divided between the two centers. Thus

$$\chi_i \chi_j \approx \tfrac{1}{2} S_{ij}(\chi_i^2 + \chi_j^2) \qquad (11)$$

The Smith method of population analysis is a modification of this procedure in which the cross product term is distributed so that the total charge and dipole moment of that term are preserved and, further, so that the atomic dipoles on the donor atom are also included. Thus

$$\chi_i \chi_j \approx \lambda_i \chi_i^2 + \lambda_j \chi_j^2 \qquad (12)$$

Integrating (12) over all space gives

$$\lambda_i + \lambda_j = S_{ij} \qquad (13)$$

Multiplying (12) by the dipole moment operator Z (measured from the donor to the metal atom) gives

$$\lambda_i 2ab \int \chi_{2s} Z \chi_{2p} d\tau + R\lambda_j = a\int \chi_j Z \chi_{2s} d\tau + b\int \chi_j Z \chi_{2p} d \qquad (14)$$

where χ_j is the metal wave function and $\chi_i = a\chi_{2s} + b\chi_{2p}$ and R is the internuclear distance. To account for the atomic dipoles on the donor, it is assumed that

$$\chi_{2s}\chi_{2p} = \lambda_D \chi_{2p}^2 + \lambda_m \chi_j^2 \qquad (15)$$

This is integrated over all space and then multiplied by the dipole moment operator Z and integrated to give

$$\lambda_m = (2ab/R)\int \chi_{2s} Z \chi_{2p} d \quad \text{and} \quad \lambda_D' = 1 - \lambda_m \qquad (16)$$

The 2p orbital was used for the donor wave function since the product $\chi_{2s}\chi_{2p}$ has the appearance of a p wave function. The donor portion of the cross product term could have been distributed between the 2s and 2p orbitals; however, no attempt was made to do this because the electron density was removed from the 2s and 2p orbitals and the ratio s/p was kept constant. The same procedure was followed for analyzing the pi symmetry terms. It must be noted that this derivation involves only two center orbitals whereas the orbitals in this investigation are group orbitals. This, however, is easily handled as the various integrals may readily be transformed (by group theoretical procedures)[1] into group integrals either before or after the various λ's have been determined. After having done this, approximations (12) and (14) are substituted into eq. (10), and the same procedure as for the Mulliken method is followed.

The procedure for transforming the dipole moment integrals into two center overlap integrals is found in Appendix II. In Table 2 the numerical values of the various weighting factors (λ's) are tabulated. (The figures in the column headed hybrid are the λ's of eq. (16).)

Self-consistency procedure

Since the coulomb and hence the resonance integrals are dependent upon the electron population and hence the charges, it is necessary to make an iterative calculation. Populations of the d, s, and p orbitals on the metal are assumed, and from these the charges are calculated. The populations and charges determine the coulomb integrals and, consequently, the resonance integrals. This information together with the group overlap integrals is then substituted into the secular determinant (eq. 1) and the eigenvalues and eigenvectors calculated. Subsequently, the eigenvectors are analyzed and the populations of the d, s, and p orbitals calculated. If the assumed and calculated populations differ by more than a predetermined amount (maximum was 0.001), new populations are assumed, and the entire procedure is repeated.

A computer program was written by the author to carry out this procedure. Eight forms of this program were used during this investigation. A copy of one of these programs is in Appendix III. The modifications that are necessary

TABLE 2

WEIGHTING COEFFICIENTS FOR THE SMITH POPULATION ANALYSIS

Metal Atom Donor Atom	Dist. (A°)	a_{1g}	e_g	t_{1u}	$t_{1u}(\pi)$	t_{2g}	Hybrid
Fe^{1+}	2.17	0.04765	0.02716	0.03857	0.03085	0.01853	0.14952
0		0.23144	0.07376	0.37252	0.10636	0.02957	0.85048
Fe^{2+}	2.17	0.04765	0.02329	0.05522	0.03405	0.01479	0.14952
0		0.23144	0.05242	0.33900	0.08162	0.01993	0.85048
Fe^{3+}	2.17	0.04765	0.01948	0.06225	0.03304	0.01166	0.14952
0		0.23144	0.03677	0.29003	0.06264	0.01338	0.85048
Fe^{1+}	2.08	0.04923	0.02897	0.03534	0.03365	0.02175	0.15599
0		0.24699	0.08607	0.38841	0.11700	0.03590	0.84401
Fe^{2+}	2.08	0.04923	0.02181	0.05389	0.03826	0.01762	0.15599
0		0.24699	0.06598	0.36640	0.09276	0.02462	0.84401
Fe^{3+}	2.08	0.04923	0.02165	0.06289	0.03786	0.01407	0.15599
0		0.24699	0.04460	0.32165	0.07288	0.01679	0.84401
Co^{o}	2.08	0.05229	0.03036	0.00945	0.01600	0.02390	0.15599
0		0.24357	0.10035	0.27949	0.11572	0.04320	0.84401
Co^{1+}	2.08	0.05229	0.02696	0.03931	0.03502	0.01948	0.15599
0		0.24357	0.07318	0.38891	0.11348	0.02968	0.84401
Co^{2+}	2.08	0.05229	0.02325	0.05697	0.03851	0.01564	0.15599
0		0.24357	0.05263	0.35684	0.08800	0.02028	0.84401
Co^{1+}	1.98	0.05413	0.02869	0.03460	0.03862	0.02330	0.16387
0		0.26172	0.08723	0.40731	0.12642	0.03704	0.83613
Co^{2+}	1.98	0.05413	0.02537	0.05430	0.04385	0.01900	0.16387
0		0.26172	0.06412	0.38866	0.10157	0.02578	0.83613
Co^{3+}	1.98	0.05413	0.02203	0.06479	0.04358	0.01541	0.16387
0		0.26173	0.04693	0.34400	0.08015	0.01801	0.83613
Co^{3+}	1.93	0.05483	0.02308	0.06374	0.04690	0.01706	0.16811
0		0.27051	0.05220	0.36306	0.08708	0.02045	0.83189
Ni^{1+}	2.08	0.07322	0.02837	0.01103	0.01762	0.02162	0.15599
0		0.12299	0.08785	0.29371	0.11829	0.03596	0.84401

TABLE 2 - Continued

Metal Atom Donor Atom	Dist. (A°)	a_{1g}	e_g	t_{1u}	$t_{1u}(\pi)$	t_{2g}	Hybrid
Ni^{2+}	2.08	0.07322	0.02501	0.04245	0.03596	0.01745	0.15599
O		0.12299	0.06232	0.38765	0.11036	0.02462	0.84401
Ni^{3+}	2.08	0.07322	0.02317	0.06007	0.03857	0.01396	0.15599
O		0.12299	0.04473	0.34453	0.08246	0.01686	0.84401
Co^{1+}	2.10	0.08241	0.02966	0.05964	---	---	0.19458
N		0.26050	0.08328	0.39167	---	---	0.80452
Co^{2+}	2.10	0.08241	0.02592	0.07386	---	---	0.19458
N		0.26050	0.06149	0.38346	---	---	0.80452
Co^{2+}	2.00	0.08669	0.02693	0.06976	---	---	0.20431
N		0.27465	0.07335	0.40982	---	---	0.79569
Co^{3+}	2.00	0.08669	0.02374	0.07858	---	---	0.20431
N		0.27465	0.05502	0.37730	---	---	0.79569
Ni^{1+}	2.06	0.08762	0.02804	0.06067	---	---	0.19836
N		0.26482	0.07680	0.39988	---	---	0.80164
Ni^{2+}	2.06	0.08762	0.02452	0.07577	---	---	0.19836
N		0.26482	0.05702	0.38608	---	---	0.80164

for different metal or donor atoms are indicated. The program incorporates a subroutine (JACFUL) written by F. Prosser[26] to diagonalize the secular determinant. It is to be noted that after one cycle, the new assumed metal orbital populations (if necessary) are the average of the previously assumed (input) and the calculated (output) metal populations. For successive iterations the input and output populations are compared. If the difference is less than 0.001 then nothing is done. If the difference between the input and output is larger than the difference of the input and output from the previous iteration then the new input is the average of the input from the previous iteration and the present iteration. If the new difference is less than the old difference but greater than 0.001, then the new input is the average of the present input and output metal orbital populations. This procedure gave rapid convergence in most instances and was more satisfactory than a straight cyclic procedure in which the output populations of one cycle are used as input for the next cycle. The straight cyclic procedure was slower to converge and occasionally gave large oscillations which made it difficult or impossible to reach self-consistency. The few cases where the procedure described above failed to give self-consistency are indicated (by a's) in Table 3 and discussed below.

RESULTS AND DISCUSSION

The calculated values for 10Dq, which is the difference in energies of the t_{2g}^* (or t_{2g} when pi bonding is omitted) and the e_g^* molecular orbital levels, are summarized for the eight different methods indicated by the column headings in Table 3. The complete self-consistent results are listed in Appendix IV in Table 9 to Table 17.

An inspection of Table 3 reveals that certain methods did not give satisfactory results (indicated by a's and b's). These are the Ballhausen-Gray-Smith method which leads to divergence and, when pi bonding is included, both methods which use the Mulliken population analysis. These four methods must be rejected for reasons given below.

One of the reasons that the Ballhausen-Gray-Smith method sometimes diverges lies in the method of estimating the resonance integral. Fenske[9] has pointed out that in using the Ballhausen-Gray approximation if the absolute value of one of the coulomb integrals is much greater than the other, the energy of the antibonding orbital is drastically affected while the energy of the bonding orbital is of essentially the same energy as the energy of the lowest coulomb integral. This causes the eigenvector of the antibonding orbital to have a large percentage metal character,

TABLE 3

SUMMARY OF CALCULATED 10Dq VALUES (CM^{-1}) FOR THE INDICATED COMPLEXES AT SELF-CONSISTENCY

Complex	Wavefunction	No Pi				Pi			
		B S	B M	W S	W M	B S	B M	W S	W M
$[Fe(H_2O)_6]^{2+}$	q = 1	a	28,210	17,970	26,170	a	16,040	16,060	19,600
	2	a	17,100	10,040	15,500	a	8,580	9,040	11,120
	3	3,270	10,320	5,520	9,220	2,960	b	5,000	6,000
$[Fe(H_2O)_6]^{3+}$	1	36,020	53,880	37,550	50,090	23,600	b	28,040	28,360
	2	22,190	35,340	22,500	32,310	14,280	b	16,710	b
	3	13,280	23,570	13,210	21,300	8,340	b	9,730	b
$[Cr(H_2O)_6]^{2+}$	0	a	48,420	30,280	46,840	a	26,870	26,870	32,510
	1	a	29,270	17,710	26,630	a	14,750	15,800	19,300
	2	a	18,140	10,100	16,110	a	7,170	9,070	10,960
$[Co(H_2O)_6]^{3+}$	1	35,700	48,230	37,880	45,720	25,140	55,400	29,040	58,820
	2	22,240	32,160	23,000	29,940	14,880	b	17,490	6,940
	3	13,760	21,830	13,930	20,100	8,360	b	10,390	22,550
$[Ni(H_2O)_6]^{2+}$	0	a	42,430	24,470	40,150	a	11,580	21,830	21,560
	1	a	25,120	13,790	22,370	a	b	12,340	11,800
	2	a	15,910	7,850	13,840	a	b	7,060	1,525
$[Co(NH_3)_6]^{2+}$	1	a	32,670	15,300	28,980	-	-	-	-
	2	a	21,380	9,130	18,400	-	-	-	-
$[Co(NH_3)_6]^{3+}$	2	19,980	34,050	21,650	31,370	-	-	-	-
	3	12,900	24,130	13,550	22,060	-	-	-	-

TABLE 3 - Continued

Complex	Wavefunction	No Pi				Pi			
		B S	B M	W S	W M	B S	B M	W S	W M
$[Ni(NH_3)_6]^{2+}$	1	a	26,420	13,260	25,550	-	-	-	-
	2	a	17,380	8,010	16,510	-	-	-	-
$[Co(H_2O)_6]^{2+}10Dq'$	2	-	-	10,070	16,800	-	-	9,030	11,060
$[Co(H_2O)_6]^{3+}10Dq'$	2	-	-	23,360	31,830	-	-	17,450	14,190
$[Co(H_2O)_6]^{3+}$alt.	3	13,800	21,900	13,900	20,100	8,200	b	10,300	b
$[Co(H_2O)_6]^{3+}$alt. 1.93 A^o	3	15,800	24,800	16,300	22,900	10,500	b	12,200	b

B: Ballhausen and Gray; W: Wolfsberg and Helmholz - Resonance integral approximations.

S: Smith; M: Mulliken - Population analysis methods.

[a]Diverges.

[b]Energy of the pi orbital on the donor atom is above the energy of a d orbital on the metal atom.

-: Not calculated.

and as a consequence, the metal has a high electron density. The Smith population analysis heightens this effect (by giving more electron density to the metal than does the Mulliken analysis) so that when these antibonding orbitals are occupied (as in iron(II), cobalt(II), and nickel(II)), there is such a high electron density on the metal that its coulomb integral becomes positive before self-consistency is achieved, and the calculations, therefore, diverge.

When pi bonding is included and the Mulliken method of population analysis is used the results often do not correspond to physical reality. This is because a scrambling of the molecular orbital energy levels has occurred and the highest and next highest energy levels which are occupied are respectively a t_{2g}^* and a t_{iu}^* molecular orbitals rather than an e_g^* and a t_{2g}^*. This means that the (predicted) lowest energy transition is permitted whereas the observed transition is of such low intensity that it is taken to be a forbidden transition.

The reason for this behavior may be understood by inspecting the Mulliken population analysis. In this method the majority of the electron density in the bond is given to the donor atom since $C_D^2 > C_M^2$ (c.f. eq. (10)). If we start with a neutral metal atom and the charge of the complex distributed over the donor atoms, then, after a few iterations, the use of the Mulliken analysis gives an

appreciable positive charge to the metal causing the coulomb integral to be low, and at the same time the decreased positive charge on the donor atom causes its coulomb integral to be high compared with the initial values. Often in the present calculations, the two coulomb integrals became essentially equal and the scrambling described above occurred.

There are four methods remaining from which a best method should be chosen, preferably one which is applicable to all types of complexes. Three of these methods exclude pi bonding while only one method includes pi bonding. From an inspection of the total energies (sum of one-electron energies) of the complexes as calculated by the various methods (Appendix IV), it is apparent that the inclusion of pi bonding lowers the total energy of the aquo complexes by approximately 2000 kK (250 eV) for the iron complexes, 1200 kK (150 eV) for the cobalt complexes, and 400 kK(50 eV) for the nickel complex. This means that there is an appreciable mixing of the pi symmetry orbital from the ligand with the metal orbitals, and hence, pi bonding should be included. Thus a best method, of those which were tried, has been found -- the Wolfsberg and Helmholz approximation for the resonance integral coupled with the Smith method of population analysis. It is necessary to add at this point that although the total energy is a minimum when self-consistency is achieved, a particular iteration may result in a lower

total energy than that obtained from one or more succeeding iterations. It may also be noted that the Wolfsberg-Helmholz-Smith method does not give the lowest total energy of those methods which include pi bonding. However, these other methods have been eliminated as a result of previous considerations.

It is now necessary to compare the calculated values for 10Dq with those which have been experimentally determined. The experimental values are[11] $[Fe(H_2O)_6]^{2+}$ 10,400 cm^{-1}, $[Fe(H_2O)_6]^{3+}$ 13,700 cm^{-1}, $[Co(H_2O)_6]^{2+}$ 9,700 cm^{-1}, $[Co(H_2O)_6]^{3+}$ 19,100 cm^{-1}, $[Ni(H_2O)_6]^{2+}$ 8,500 cm^{-1}, $[Co(NH_3)_6]^{2+}$ 10,500 cm^{-1}, $[Co(NH_3)_6]^{3+}$ 23,500 cm^{-1}, and $[Ni(NH_3)_6]^{2+}$ 10,800 cm^{-1}.

From an inspection of Table 3 it is apparent that almost any value of 10Dq may be obtained depending on the choice of the charge (q) of the free ion metal wave function. The next question is, "Is it possible to chose q empirically so that starting from this one piece of information, for each metal, it is possible to determine all of its experimental 10Dq values?" In order to do this it is necessary to refer to Figures 2 through 5 where log 10Dq is plotted as a function of the log of r_o, the radius of maximum probability of the 3d orbitals. These radii of maximum probability are tabulated in Table 4. They were obtained

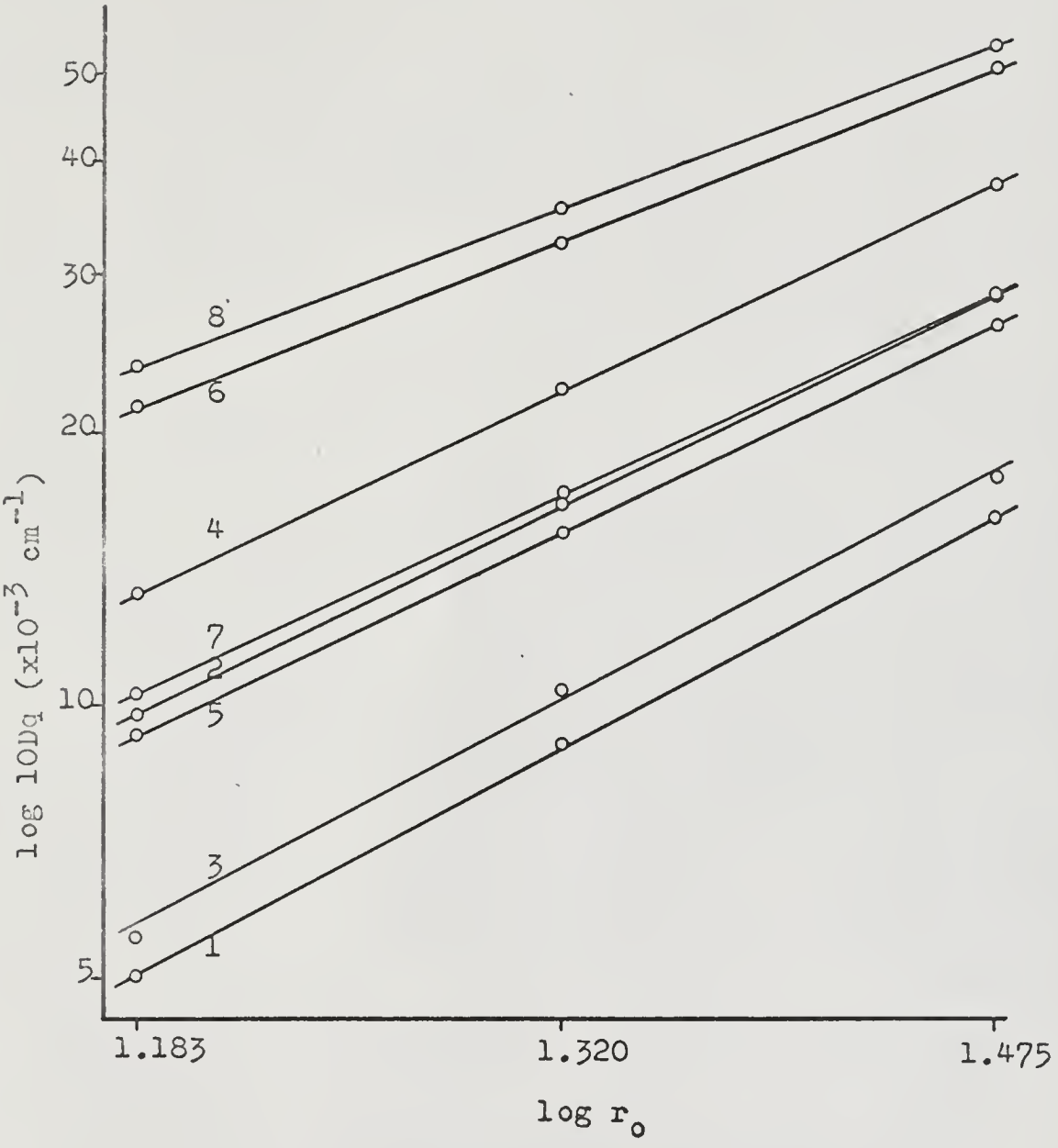

Fig. 2.-Log 10Dq vs log r_o for the iron-aquo complexes. Odd numbers are Fe^{2+}, even numbers are Fe^{3+}; 1 + 2 W S Pi included, 3 + 4 W S No Pi, 5 + 6 W M No Pi, 7 + 8 B M No Pi.

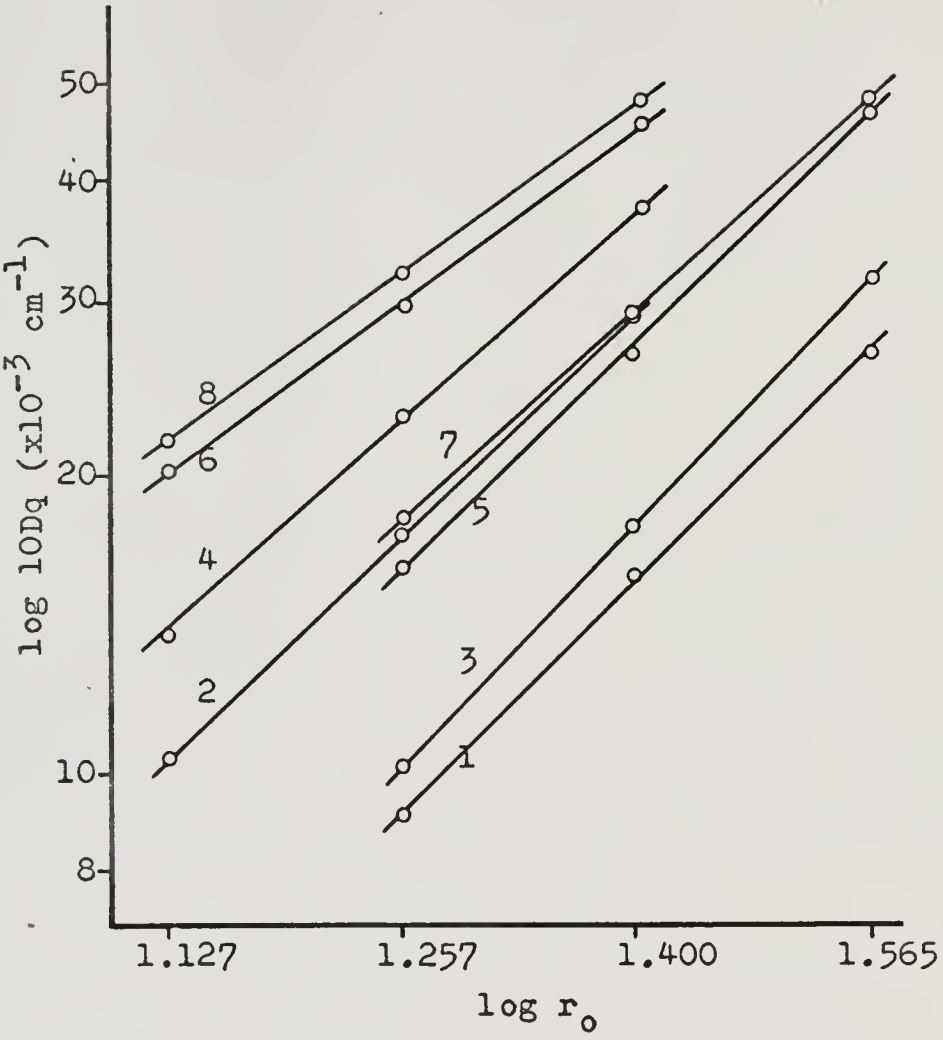

Fig. 3.-Log 10Dq vs log r_o for the cobalt-aquo complexes. Odd numbers are Co^{2+}, even numbers are Co^{3+};1 + 2 W S Pi, 3 + 4 W S No Pi, 5 + 6 W M No Pi, 7 + 8 B M No Pi.

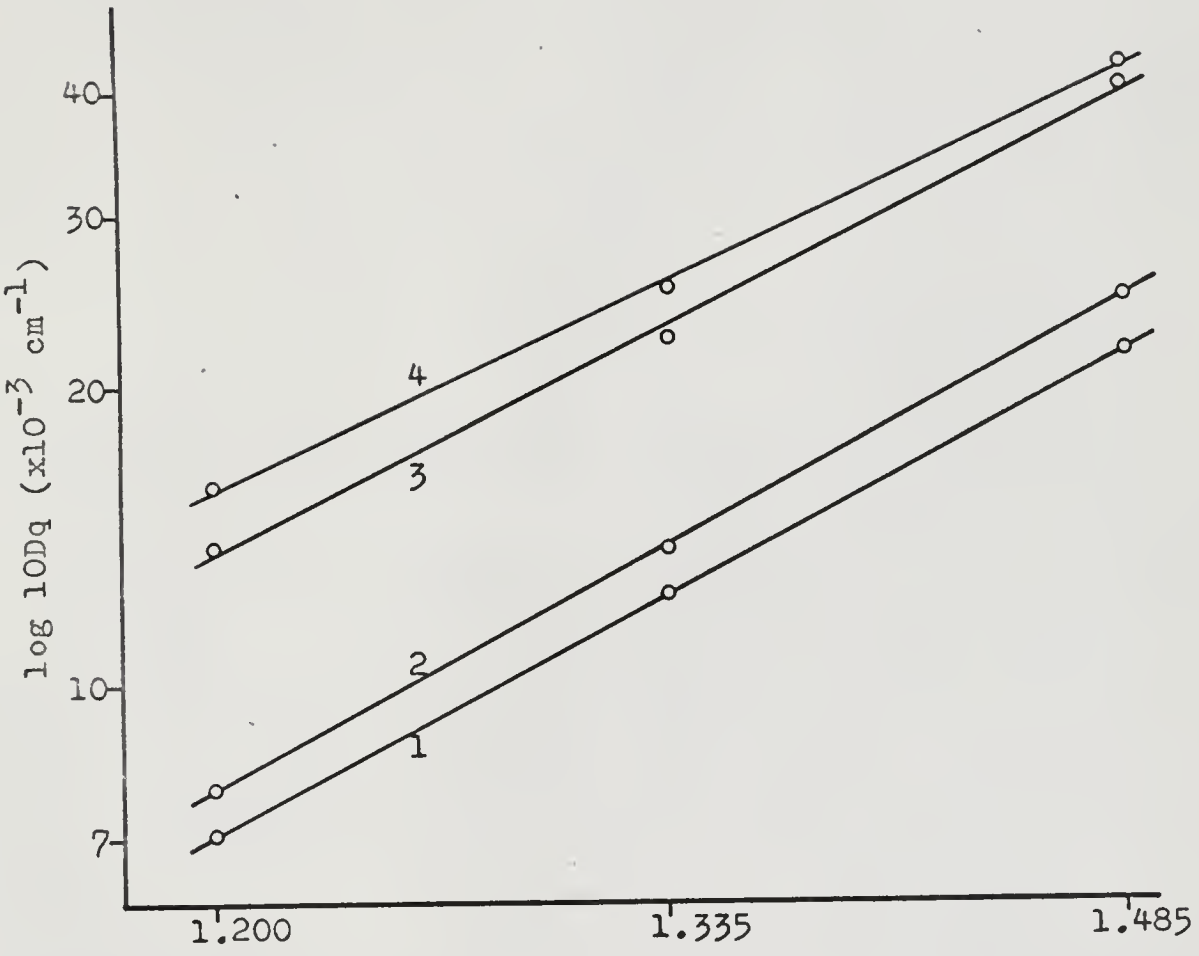

Fig. 4.-Log 10Dq vs log r_o for $[Ni(H_2O)_6]^{2+}$.
1 W S Pi, 2 W S No Pi, 3 W M No Pi, 4 B M No Pi.

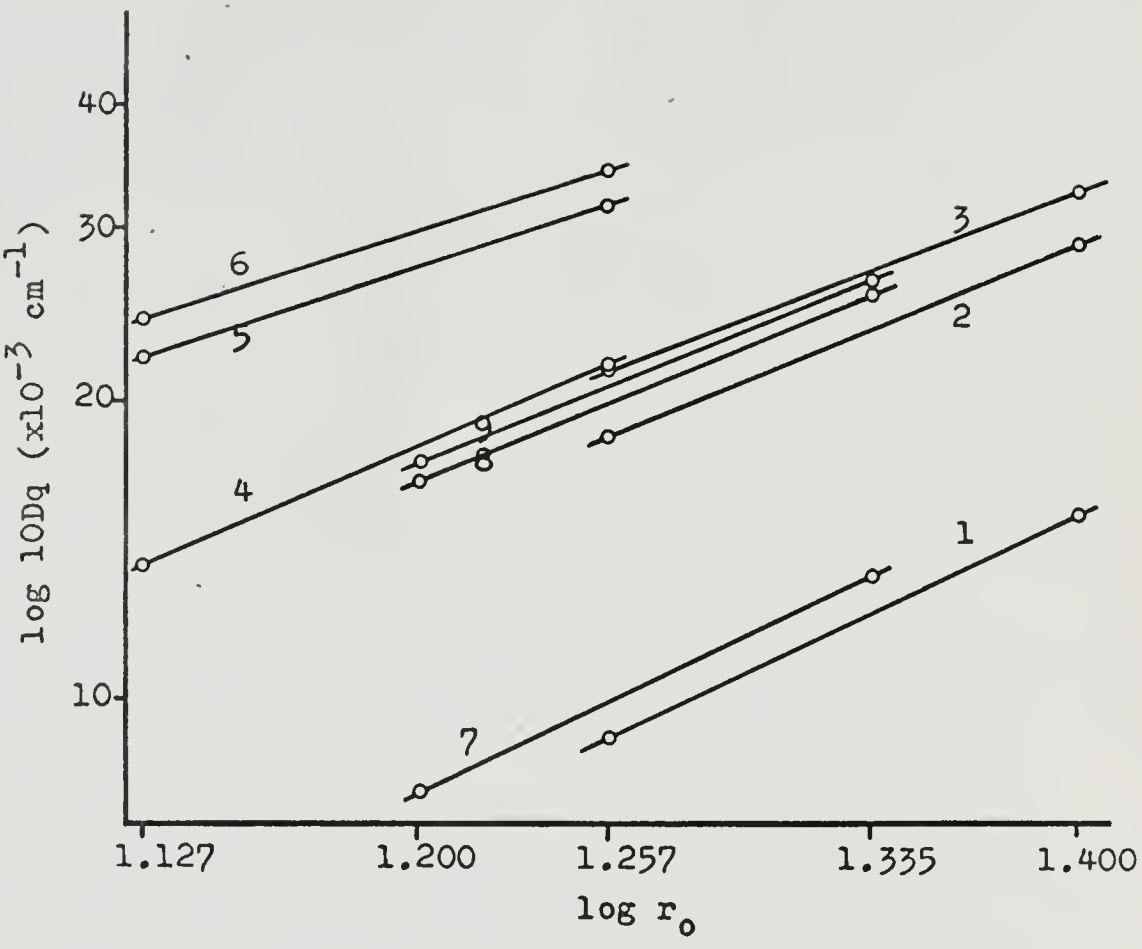

Fig. 5.-Log 10Dq vs log r_o for the cobalt and nickel ammine complexes. 1,2,3 Co^{2+}; 4,5,6 Co^{3+}; 7,8,9 Ni^{2+}; 1,4,7 W S; 2,5,8 W M; 3,6,9 B M.

by plotting $r^2[R(r)]^2$ as a function of r (where r is the radius of the wave function and R (r) is the radial portion of the 3d wave function) and visually picking the maximum of $r^2\ [R(r)]^2$.

TABLE 4

RADII OF MAXIMUM PROBABILITY (r_o) FOR IRON, COBALT AND NICKEL (Å)

Metal Atom q =	0	1	2	3
Fe	-	1.475	1.320	1.183
Co	1.565	1.400	1.257	1.127
Ni	1.485	1.335	1.200	-

It was empirically determined that a plot of log 10Dq vs log r_o gives a good straight line for all of the results, and it is of interest to note that all of these lines have virtually the same slope.

Since it has been determined that the Wolfsberg and Helmholz resonance integral approximation coupled with the Smith population analysis (pi bonding included) gives the best results in terms of its ability to handle pi bonding, this method will be used in an attempt to extrapolate from a single starting point for each metal atom, all of the observed 10Dq values. Let the double charged aquo complexes be used as this starting point. It is observed (Appendix

IV) that although there is a gradual increase in self-consistent charges as q increases (that is, as the size of the metal wave function decreases), there is a large difference between the self-consistent charges Z on the metal atoms of the doubly charged and triply charged complexes regardless of which q is used. If it is assumed that the self-consistent charge Z is independent of q and an average is taken over Z for the three values of q, then it is possible to determine how much the wave functions of the complexes have shrunk in loosing one electron, that is, the increase in q on going from a doubly to a triply charged complex. Further, it is assumed that the radius of maximum probability which gives the experimental 10Dq values for the doubly charged aquo complexes is equal to the radius r_o of the metal atom in this complex and more important corresponds to Z, the average of the calculated self-consistent charges. These charges Z are all approximately zero while the radius of the free metal ion 3d orbital which gives the experimental 10Dq corresponds to a charge q of approximately two for the free atom wave function. Thus the free atom wave functions shrink when the complex is formed.

The value of q for the self-consistent complexes is assumed to be larger or smaller than q_o, the value of q for the doubly charged aquo complexes, by the difference (ΔZ) in the average of the calculated self-consistent charges

of the two complexes (that is, $q = q_o + \Delta Z$). When this charge adjustment is made, the 10Dq values listed in Table 5 are predicted.

TABLE 5

PREDICTED 10Dq VALUES USING THE DOUBLY CHARGED AQUO COMPLEXES AS STANDARDS

Complex (Experimental 10Dq)		Pi		No Pi	
		W S	W S	W M	B M
$[Fe(H_2O)_3]^{2+}$ standard	Z	0.06	0.09	0.75	1.02
	10Dq	10,400	10,400	10,400	10,400
$[Fe(H_2)_6]^{3+}$ (13,700 cm^{-1})	Z	0.60	0.74	1.09	1.27
	10Dq	14,200	16,700	20,000	21,000
$[Co(H_2O)_6]^{2+}$ standard	Z	-0.04	-0.01	0.70	0.96
	10Dq	9,700	9,700	9,700	9,700
$[Co(H_2O)_6]^{2+}$ (19,100 cm^{-1})	Z	0.59	0.63	0.93	1.14
	10Dq	13,600	16,400	18,700	18,000
$[Co(NH_3)_6]^{2+}$ (10,500 cm^{-1})	Z	a	-0.45	0.38	0.61
	10Dq	11,500	11,000	13,900	13,400
$[Co(NH_3)_6]^{3+}$ (23,500 cm^{-1})	Z	a	0.20	0.58	0.76
	10Dq	20,500	19,000	23,400	25,000
$[Ni(H_2O)_6]^{2+}$ standard	Z	-0.04	-0.02	0.76	1.00
	10Dq	8,500	8,500	8,500	8,500
$[Ni(NH_3)_6]^{2+}$ (10,800 cm^{-1})	Z	a	-0.49	0.29	0.41
	10Dq	11,800	10,800	13,900	13,500

[a]Using the self-consistent charge of W S no pi.

Several observations may be made on the results presented in this table. The most apparent of these is that the so-called best method selected above does not extrapolate with good agreement to the experimental 10Dq values of cobalt(III). However, reasonable agreement is obtained for the other complexes (within 10%). It is also apparent that it is possible to extrapolate with almost as good over-all agreement using the methods which do not include pi bonding but are acceptable except for the total energy arguments. An observation on the self-consistent charges is that in going from the aquo to the ammine complexes the metal wave functions shrink and, in the extrapolating procedure, produce a larger 10Dq value for the ammine complexes than for the aquo complexes in agreement with experiment. This is also in qualitative agreement with arguments based upon the cloud expanding power of the nephelauxetic series.

However, several other factors become apparent upon closer scrutiny. With the Wolfsberg-Helmholz-Smith method it is possible to extrapolate to acceptable estimates of the experimental 10Dq values so long as the spin multiplicity does not decrease. From iron(II) to iron(III) the extrapolation is from quintet to sextet spin multiplicity but the difficulty arises in going from high-spin cobalt(II) to low-spin cobalt(III). Unfortunately, the extrapolated

estimate is lower than the experimental value and any attempt to correct for this change in spin multiplicity will decrease the predicted 10Dq values. The correction which could be applied is to subtract the pairing energy of cobalt(III) (21,000 cm^{-1} for the free ion) from the predicted 10Dq.

Another observation that can be made is that the Wolfsberg-Helmholz-Mulliken method with pi bonding omitted does extrapolate with excellent agreement from high-spin to low-spin cobalt complex but does not give very good agreement when the spin multiplicity remains constant. However, no significance was attached to this observation since it is desired to have a single method for the treatment of all complexes. A correction factor could conceivably be applied to bring all of these predicted 10Dq values into agreement with the experimental values but a different correction factor could, with as much justification, be applied to the Wolfsberg-Helmholz-Smith method and the total energy arguments above strongly suggest that pi bonding should be included.

It must be added at this point that if the doubly charged ammines of cobalt or nickel had been chosen as the reference compounds, the extrapolation would not have been as good as the above results. It may be that the cause of this is that it is necessary to start with the weaker ligand field and extrapolate to the stronger field strength. Future work with other ligands should clarify this point.

In the procedure section it was stated that an alternant procedure for estimating the coulomb integral of the donor atom was used in order to determine the sensitivity of the experimental parameters to the magnitude of this estimate. This alternant procedure raises the coulomb integral of the donor by approximately 2000 cm^{-1} (0.25 eV) but, as is apparent from Table 3, has little effect on 10Dq. (The change is less than 200 cm^{-1}.) Further, the self-consistent charges, the total energies, and the metal orbital populations are essentially the same for both procedures (c.f. Table 12 and Table 17 of Appendix IV).

However, under certain conditions the estimate for the coulomb integral does become important. This is evidenced by a comparison of the present results with those of Cotton and Haas,[7] who used the Ballhausen-Gray-Mulliken scheme, but with coulomb integrals much smaller than those of this investigation. For example, for $[Co(NH_3)_6]^{2+}$ Cotton and Haas find 10Dq = 10,910 cm^{-1} using a d coulomb integral of -63,250 cm^{-1}. Our estimate for the coulomb integral is -154,810 cm^{-1}, which gives 10Dq = 32,670 cm^{-1}, but we cannot reproduce their coulomb integrals.

As a test of the sensitivity of the experimental parameters to the internuclear distance, the $[Co(H_2O)_6]^{3+}$ ion was treated (with the alternant donor atom coulomb integral estimate) using an internuclear distance of 1.93 Å.

This is 0.05 Å less than the distance arrived at in the first section of the procedure. However, this difference should be much greater than the error in the first estimate. Table 3 shows that, although the 10Dq values are raised by approximately 2000 cm^{-1}, the shortened internuclear distance does not affect any of the conclusions concerning the various methods. With reference to the extrapolation of Table 5 it is apparent that the increase in 10Dq caused by the decreased distance is in the right direction and would improve the extrapolation for the Wolfsberg-Helmholz-Smith method but is not a sufficient shift to cause the extrapolation to give agreement within 10 per cent.

To this point, the 10Dq results have all been obtained by using Koopmans' theorem, that is, the observed transitions are said to be equal to the difference in the energies of the one electron molecular orbitals. If instead of this procedure, the total energies of the self-consistent ground and first excited states are calculated, then the difference in these two energies should be equal to the first observed transition (10Dq').

In Table 6 are listed 10Dq' values that were calculated in this manner. All calculations use the free atom doubly charged wave functions for cobalt. The first observed transition for $[Co(H_2O)_6]^{2+}$ is the $^4T_{1g} \rightarrow {}^4T_{1g}(F)$ transition

TABLE 6

10Dq' VALUES FOR THE AQUO COMPLEXES OF COBALT(II) AND (III) (CM^{-1})

Complex	No Pi		Pi	
	W S	W M	W S	W M
$[Co(H_2O)_6]^{2+}$	12,650	11,200	11,500	20,930
$[Co(H_2O)_6]^{3+}$	14,960	9,150	30,510	82,450

and is observed at 8,100 cm^{-1}. For $[Co(H_2O)_6]^{3+}$ this transition is the $^1A_{1g} \rightarrow {}^1T_{1g}$ transition which is observed at 16,600 cm^{-1}.

If it is assumed that 10Dq' depends upon the size of the wave function in the same manner as does 10Dq then it should be possible to use the first observed transition of one of the complexes as a standard and extrapolate to the observed 10Dq' value of the other complex. If this is done using the observed 10Dq' value for $[Co(H_2O)_6]^{2+}$ as a standard, the predicted 10Dq' value for $[Co(H_2O)_6]^{3+}$ is 16,000 cm^{-1} in good agreement with the experimental value. This result shows that it is possible to extrapolate an experimental parameter from high-spin cobalt(II) to low-spin cobalt(III). It remains for future investigation to prove, or disprove, the general applicability of this different method.

A modification that could be applied to the Wolfsberg-Helmholz-Smith procedure in the case of cobalt(III) would be to subtract the pairing energy of cobalt(III) from the estimate of the metal d orbital coulomb integral. This procedure would correct for the change in spin multiplicity encountered in extrapolating from cobalt(II) to cobalt(III). Qualitatively this modification will improve the extrapolation since 10Dq is increased if the metal orbital coulomb integral is decreased. However, no calculations have been made using this modification.

SUMMARY

The hexaamine complexes of cobalt and nickel have been subjected to four different methods of approximate molecular orbital calculations and the hexaaquo complexes of iron, cobalt, and nickel to eight methods. For the aquo complexes pi symmetry orbitals on the donor atoms have been treated as bonding and as non-bonding orbitals. Several different free atom wave functions have been used for each complex. The effect of changing the estimate for the donor atom coulomb integral and the effect of changing the internuclear separation have also been investigated.

The results indicate that the method which uses the Wolfsberg and Helmholz approximation for the resonance integral and the Smith method of population analysis is the preferred method, and further the results indicate that pi bonding should be included when pi symmetry orbitals are available. Using this method, it is possible to choose appropriate metal wave functions semi-empirically and extrapolate to 10Dq values of other compounds with good agreement unless the spin multiplicity is decreased. In such a case a modified procedure is necessary and several methods have been proposed.

APPENDICES

APPENDIX I

The generalized linear combinations used for calculating the valence state ionization potentials (VSIP's) for the metal atoms and their generalized solutions for the coefficients are as follows:

For the VSIP of a d electron

$$a(d^{n-Z}) + b(c^{n-1-Z_s}) + c(d^{n-1-Z_p}) = d^{\alpha}s^{\beta}p^{\gamma}$$

$$a = [\alpha-\beta(n-1-Z) - \gamma(n-1-Z)]/(n-Z)$$

$$b = \beta$$

$$c = \gamma$$

For the VSIP of an s electron

$$a(d^{n-1-Z_s}) + b(d^{n-2-Z_s^2}) + c(d^{n-2-Z_{sp}}) = d^{\alpha}s^{\beta}p^{\gamma}$$

$$a = [2\alpha + \beta(Z+2-n) + \gamma(Z+2-n)]/(n-Z)$$

$$b = [-\alpha + \beta(n-1-Z) - \gamma]/(n-Z)$$

$$c = \gamma$$

For the VSIP of a p electron

$$a(d^{n-1-Z_p}) + b(d^{n-2-Z_p^2}) + c(d^{n-2-Z_{sp}}) = d^{\alpha}s^{\beta}p^{\gamma}$$

$$a = [2\alpha + \beta(Z+2-n) + \gamma(Z+2-n)]/(n-Z)$$

$$b = [-\alpha - \beta + \gamma(n-1-Z)]/(n-Z)$$

$$c = \beta$$

where a, b and c are the coefficients of the linear combination, α, β and γ are the assumed d, s and p populations, $Z = n-\alpha-\beta-\gamma$ the charge on the metal and n = 8 for iron, 9 for cobalt and 10 for nickel.

The linear combination for the donor atoms and the generalized solutions are as follows:

$$s^v p^w = a(2s^2 2p^{n-Q}) + b(2s2p^{n+1-Q})$$

$$a = [(n+1-Q)v - w]/(n+2-Q)$$

$$b = v - 2a$$

where $v = (2-Q)C_2^2 + R_s$, $w = (2-Q)C_p^2 + R_p$, Q is the charge on each donor atom, n = 3 for nitrogen and n = 4 for oxygen. C_s, C_p, R_s and R_p are the same as in the text.

The VSIP data of Basch and Viste[3] are listed in Table 7 for the metal atoms and Table 8 for the donor atoms. The equations below were used in the computer program for calculating the VSIP's. The configuration is the initial configuration; the other letter is the electron lost. The data in Table 7 were fitted to a straight line while the data in Table 8 were fitted to a parabolic curve except in one case.

	Fe(n=8)	Co(n=9)	Ni(n=10)
d^n d	-100.0Z-41.9	-105.1Z-44.8	-109.7Z-47.6
d^{n-1} s d	-115.3Z-70.5	-120.1Z-75.6	-124.9Z-80.9
c^{n-1} p d	-115.7Z-81.2	-119.4Z-88.4	-122.4Z-95.9
d^{n-1} s s	- 71.2Z-57.3	- 73.9Z-59.1	- 74.6Z-60.8
d^{n-2} s^2s	- 80.4Z-68.3	- 82.5Z-70.5	- 84.4Z-72.3
d^{n-2} sps	- 74.7Z-81.4	- 78.6Z-84.0	- 83.0Z-86.0
d^{n-1} p p	- 58.1Z-29.9	- 59.5Z-30.7	- 60.8Z-31.4
d^{n-2} p^2p	- 65.1Z-39.7	- 68.2Z-40.7	- 71.7Z-41.6
d^{n-2} spp	- 65.1Z-40.3	- 68.2Z-40.8	- 71.7Z-40.9

	N(n=3)	O(n=4)
$2s^2 2p^n$ s	$-9.75(Q+5.65385)^2$	$-9.7(Q+6.49485)^2$
	- 105.4683	+ 148.3752
$2s2p^{n+1}$s	$-8.95(Q+5.87430)^2$	$+9.6(Q-9.20833)^2$
	- 82.8415	-1064.1166
$2s^2 2p^n$ p	$-12.6(Q+4.48016)^2$	$-12.95(Q+4.91699)^2$
	- 146.5049	+ 185.6892
$2s^2 2p^{n+1}$p	$-23.4(Q+1.58333)^2$	-147.0 Q - 126.4
	+ 70.7375	

TABLE 7

VALENCE STATE IONIZATION POTENTIAL DATA FOR IRON, COBALT AND NICKEL
(IN 1000 CM^{-1})

	Chg.	0 ⟶ +1			+1 ⟶ +2		
	n	$3d^n$	$3d^{n-1}4s$	$3d^{n-1}4p$	$3d^{n-1}$	$3d^{n-2}4s$	$3d^{n-2}4p$
Ionization of a 3d electron							
Fe	8	41.9	70.0	81.2	141.9	185.3	196.9
Co	9	44.8	75.6	88.4	149.8	195.7	207.8
Ni	10	47.6	80.9	95.9	157.3	205.8	218.3

	Chg.	0 ⟶ +1			+1 ⟶ +2		
	n	$d^{n-1}s$	$d^{n-2}s^2$	$d^{n-2}sp$	$d^{n-2}s$	$d^{n-3}s^2$	$d^{n-3}sp$
Ionization of a 4s electron							
Fe	8	57.3	68.3	81.4	128.5	148.7	156.1
Co	9	59.1	70.5	89.0	133.0	153.0	162.6
Ni	10	60.8	72.3	86.0	137.2	156.7	169.0

	Chg.	0 ⟶ +1			+1 ⟶ +2		
	n	$d^{n-1}p$	$d^{n-2}p^2$	$d^{n-2}sp$	$d^{n-2}p$	$d^{n-3}p^2$	$d^{n-3}sp$
Ionization of a 4p electron							
Fe	8	29.9	39.7	40.3	88.0		105.4
Co	9	30.7	40.7	40.8	90.2		109.0
Ni	10	31.4	41.6	40.9	92.2		112.6

TABLE 8

VALENCE STATE IONIZATION POTENTIAL FOR NITROGEN AND OXYGEN
(IN 1000 CM^{-1})

		0 → +1		+1 → +2		+2 → +3	
	N	$2s^2sp^{n-1}$	$2s2p^n$	$2s^2sp^{n-2}$	$2s2p^{n-1}$	$2s^22p^{n-3}$	$2s2p^{n-2}$
Ionization of a 2s electron							
N	4	206.2	226.0	326.2	340.1	465.7	472.1
O	5	260.8	473.3	396.5	417.3	551.6	565.3

		0 → +1		+1 → +2		+2 → +3	
	N	$2s^22p^{n-1}$	$2s2p^n$	$2s^22p^{n-2}$	$2s2p^{n-1}$	$2s^22p^{n-3}$	$2s2p^{n-2}$
Ionization of a 2p electron							
N	4	106.4	129.4	231.9	226.9	382.6	371.2
O	5	127.4	126.4	267.7	273.4	433.9	422.9

APPENDIX II

The dipole moment integrals necessary for the Smith method of population analysis may be transformed into two center overlap integrals by multiplication of a second orbital by a numerical constant. The numerical constant and the form of the second orbital, which is used for the overlap integral, are determined by the form of the product of the dipole moment operator (Z) and one of the orbitals in the dipole moment integrals. The transformations that were used in this investigation are listed below:

$$z\chi(\zeta_{200}) = \frac{1}{\zeta_{100}}\chi(\zeta^{100}_{200}) + \frac{\sqrt{10}}{2\zeta_{200}}\chi(\zeta^{200}_{310})$$

$$z\chi(\zeta_{210}) + \frac{\sqrt{2}}{\zeta_{210}}\chi(\zeta^{210}_{320}) + \frac{\sqrt{10}}{2\zeta_{210}}\chi(\zeta^{210}_{300})$$

$$z\chi(\zeta_{211}) = \frac{\sqrt{6}}{2\zeta_{211}}\chi(\zeta^{211}_{321})$$

where $\chi(\zeta_{n1m})$ is a double zeta wave functions of Clementi and $\chi(\zeta^{n1m}_{n'1'n'})$ are the wave functions of Clementi with an angular portion corresponding to the quantum numbers n', $1'$ and m' and a radial portion with the orbital exponents corresponding to the original wave function.

```
C      THIS PROGRAM IS FOR THE COBALT-OXYGEN DONOR SYSTEM WITH PI BONDING
C      INCLUDED. FOR A DIFFERENT METAL (M) OR DONOR (D) OR FOR THE EXCLU-
C      SION OF PI BONDING THE INDICATED CARDS (COLUMN 72 ) ARE ALTERED
C      OR REMOVED
       DIMENSION SA(6,6),SE(6,6),STU(6,6),STG(6,6),HA(6,6),HE(6,6),
      1HTU(6,6),HTG(6,6),D(6,6),VD(6,6),VDL(6,6),G(6,6),B(6,6),V(6,6),
      1GG(6,6),EA(6),EE(6),ETU(6),ETG(6),TITLE(24),CA(6,6),CE(6,6),CTU(6,
      16),CTG(6,6),C(6,6),SA1(36),SE1(36),STU1(36),STG1(36),HA1(36),HE1(3
      16),HTU1(36),HTG1(36),CA1(36),CE1(36),CTU1(36),CTG1(36)
       EQUIVALENCE (SA,SA1),(SE,SE1),(STU,STU1),(STG,STG1),(HA,HA1),
      1(HE,HE1),(HTU1,HTU),(HTG,HTG1),(CA,CA1),(CE,CE1),(CTU,CTU1),
      1(CTG,CTG1)
       COMMON M,KAL,KBE,KGA
   31  READ INPUT TAPE 5,900,TITLE
  900  FORMAT(12A6/12A6)
       READ INPUT TAPE 5,901,M,JOB,JMAX,BW,SM,P
  901  FORMAT(3I2,3F2.0)
       READ INPUT TAPE 5,902,WTA,ALA1,ALA2,SPA1,SPA2
       READ INPUT TAPE 5,902,WTE,ALE1,ALE2,SPE1,SPE2
       READ INPUT TAPE 5,902,WTTU,ALTU1,ALTU2,SPTU1,SPTU2
       READ INPUT TAPE 5,902,WTTUP,ALTU3,ALTU4                          NP
       READ INPUT TAPE 5,902,WTTG,ALTG1,ALTG2                           NP
  902  FORMAT(5(F10.0))
       READ INPUT TAPE 5,902,ZZ,A,BB,ROS,ROP
       READ INPUT TAPE 5,902,AL1,BE1,GA1
       READ INPUT TAPE 5,902,SA1(7),SE1(7),STU1(7),STU1(13),STG1(7)     NP
       SA1(2)=SA1(7)
       SE1(2)=SE1(7)
       STU1(2)=STU1(7)
       STU1(3)=STU1(13)
       STG1(2)=STG1(7)
       KAL=0
       KBE=0
       KGA=0
    1  JOB=JOB+1
       IF(JMAX-JOB)33,33,32
```

```
   32 Z=9.-AL1-BE1-GA1                                                    M
      Q=(ZZ-Z)/6.
      EOS1=-9.7*(Q+6.494845)**2+148.375196                                D
      EOS2=9.6*(Q-9.20833333)**2-1064.116608                              D
      EOP1=-12.95*(Q+4.916988)**2+185.689195                              D
      EOP2=-147.0*Q-126.4                                                 D
      AD=((5.-Q)* (A*(2.-Q)+ROS)-BB*(2.-Q)-ROP)/(6.-Q)                    D
      BD=A*(2.-Q)+ROS-2.*AD                                               D
      HA1(8)=A*(AD*EOS1+BD*EOS2)+BB*(AD*EOP1+BD*EOP2)
      HE1(8)=HA1(8)
      HTU1(8)=HA1(8)
      HTG1(8)=AD*EOP1+BD*EOP2
      HTU1(15)=HTG1(8)
      DO 100 I=1,M
      SA(I,I)=1.0
      SE(I,I)=1.0
      STU(I,I)=1.0
  100 SIG(I,I)=1.0
      STU1(15)=1.0
C
C     CALCULATE EVALS ETC FOR A(1G) SYMMETRY
C
      ASA=(2.*AL1+BE1*(Z-7.)+GA1*(Z-7.))/(9.-Z)                           M
      BSA=(-AL1+BE1*(8.-Z)-GA1)/(9.-Z)                                    M
      ES1=-73.9*Z-59.1                                                    M
      ES2=-82.5*Z-70.5                                                    M
      ES3=-78.6*Z-84.0                                                    M
      HA1(1)=ASA*ES1+BSA*ES2+GA1*ES3
      IF(BW)2,2,3
    2 HA1(7)=-2.*SA1(7)*SQRTF(HA1(1)* HA1(8))
      GO TO 4
    3 HA1(7)=SA1(7)*(HA1(1)+HA1(8))
    4 HA1(2)=HA1(7)
      CALL DIAG (HA,SA,EA,CA)
      IF(SM)5,5,6
    5 RSCA1=CA1(1)**2+WTA*ALA1 *CA1(1)*CA1(2)+SPA1*CA1(2)**2
```

```
      RSDA1=SPA2*CA1(2)**2+WTA*ALA2 *CA1(1)*CA1(2)
      RSCA2=CA1(7)**2+WTA*ALA1 *CA1(7)*CA1(8)+SPA1 *CA1(8)**2
      RSDA2=SPA2*CA1(8)**2+WTA*ALA2*CA1(7)*CA1(8)
      BE2=2.*RSCA2
      GO TO 7
    6 RMCA1=CA1(1)**2+SA1(7)*CA1(1)*CA1(2)
      RMDA1=CA1(2)**2+SA1(7)*CA1(1)*CA1(2)
      RMCA2=CA1(7)**2+SA1(7)*CA1(7)*CA1(8)
      RMDA2=CA1(8)**2+SA1(7)*CA1(7)*CA1(8)
      BE2=2.*RMCA2
C
C     CALCULATE EVALS ETC FOR E(G) SYMMETRY
C
    7 DD=(AL1-BE1*(8.-Z)-GA1*(8.-Z))/(9.-Z)                              M
      ED1=-105.0*Z-44.8                                                  M
      ED2=-120.1*Z-75.6                                                  M
      ED3=-119.4*Z-88.4                                                  M
      HE1(1)=DD*ED1+GA1*ED2+BE1*ED3
      IF(BW)8,8,9
    8 HE1(7)=-2.*SE1(7)*SQRTF(HE1(1)*HE1(8))
      GOTO 10
    9 HE1(7)=SE1(7)*(HE1(1)+HE1(8))
   10 HE1(2)=HE1(7)
      CALL DIAG (HE,SE,EE,CE)
      IF (SM) 11,11,12
   11 RSCE1=CE1(1)**2+WTE*ALE1*CE1(1)*CE1(2)+SPE1*CE1(2)**2
      RSDE1=SPE2*CE1(2)**2+WTE*ALE2*CE1(1)*CE1(2)
      RSCE2=CE1(7)**2+WTE*ALE1*CE1(7)*CE1(8)+SPE1*CE1(8)**2
      RSDE2=SPE2*CE1(8)**2+WTE*ALE2*CE1(7)*CE1(8)
      GO TO 13
   12 RMCE1=CE1(1)**2+SE1(7)*CE1(1)*CE1(2)
      RMDE1=CE1(2)**2+SE1(7)*CE1(1)*CE1(2)
      RMCE2=CE1(7)**2+SE1(7)*CE1(7)*CE1(8)
      RMDE2=CE1(8)**2+SE1(7)*CE1(7)*CE1(8)
C
C     CALCULATE EVALS ETC FOR T(2G) SYMMETRY
```

```
C
   13 HTG1(1)=HE1(1)
      IF(BW) 14,14,15
   14 HTG1(7)=-2.*STG1(7)*SQRTF(HTG1(1)*HTG1(8))
      GOTO 16
   15 HTG1(7)=STG1(7)*(HTG1(1)+HTG1(8))
   16 HTG1(2)=HTG1(7)
      CALL DIAG (HTG,STG,CTG,CTG)
      IF(SM) 17,17,18
   17 RSCTG1=CTG1(1)**2+WTTG*ALTG1*CTG1(1)*CTG1(2)
      RSDTG1=      CTG1(2)**2+WTTG*ALTG2*CTG1(1)*CTG1(2)
      RSCTG2=CTG1(7)**2+WTTG*ALTG1*CTG1(7)*CTG1(8)
      RSDTG2=      CTG1(8)**2+WTTG*ALTG2*CTG1(7)*CTG1(8)
      AL2=4.*RSCE2+P*RSCE1+(9.-ZZ-P)*RSCTG1+6.*RSCTG2                    NP
      GO TO 19
   18 RMCTG1=CTG1(1)**2+CTG1(1)*CTG1(2)*STG1(7)
      RMDTG1=CTG1(2)**2+STG1(7)*CTG1(1)*CTG1(2)
      RMCTG2=CTG1(7)**2+STG1(7)*CTG1(7)*CTG1(8)
      RMDTG2=CTG1(8)**2+STG1(7)*CTG1(7)*CTG1(8)
      AL2=RMCE2*4.+P*RMCE1+(9.-ZZ-P)*RMCTG1+6.*RMCTG2                    NP
C
C     CALCULATE EVALS ETC FOR T(1U) SYMMETRY
C
   19 AP=(2.*AL1+BE1*(Z-7.)+GA1*(Z-7.))/(9.-Z)                          M
      BP=(-AL1-BE1+GA1*(8.-Z))/(9.-Z)                                   M
      EP1=-59.5*Z-30.7                                                  M
      EP2=-68.2*Z-40.7                                                  M
      EP3=-68.2*Z-40.8                                                  M
      HTU1(1)=AP*EP1+BP*EP2+BE1*EP3
      IF(BW)20,20,21
   20 HTU1(7)=-2.*STU1(7)*SQRTF(HTU1(8)*HTU1(1))
      HTU1(13)=-2.*STU1(13)*SQRTF(HTU1(1)*HTU1(15))
      GOTO 22
   21 HTU1(7)=STU1(7)*(HTU1(1)+HTU1(8))
      HTU1(13)=STU1(13)*(HTU1(1)+HTU1(15))
   22 HTU1(2)=HTU1(7)
```

```
      HTU1(3)=HTU1(13)
      M=M+1                                                              NP
      CALL DIAG (HTU,STU,ETU,CTU)
      M=M-1                                                              NP
      IF(SM) 23,23,24
   23 RSCTU1=CTU1(1)**2+WTTU*ALTU1*CTU1(1)*CTU1(2)+SPTU1*CTU1(2)**2
     1+WTTUP*ALTU3*CTU1(1)*CTU1(3)                                       NP
      RSDTU1=SPTU2*CTU1(2)**2+WTTU*ALTU2*CTU1(1)*CTU1(2)+CTU1(3)**2      NP
     1+WTTUP*ALTU4*CTU1(1)*CTU1(3)                                       NP
      RSCTU2=CTU1(7)**2+WTTU*ALTU1*CTU1(7)*CTU1(8)+SPTU1*CTU1(8)**2
     1+WTTUP*ALTU3*CTU1(7)*CTU1(9)                                       NP
      RSDTU2=SPTU2*CTU1(8)**2+WTTU*ALTU2*CTU1(7)*CTU1(8)
     1+CTU1(9)**2+WTTUP*ALTU4*CTU1(7)*CTU1(9)                            NP
      RSCTU3=CTU1(13)**2+WTTUP*ALTU1*CTU1(13)*CTU1(14)+CTU1(14)**2       NP
     1*SPTU1+WTTUP*ALTU3*CTU1(13)*CTU1(15)                               NP
      RSDTU3=SPTU2 *CTU1(14)**2+CTU1(15)**2+WTTU*ALTU2*CTU1(13)*CTU1(14)NP
     1+WTTUP*ALTU4*CTU1(13)*CTU1(15)                                     NP
      GA2=6.*RSCTU2+6.*RSCTU3                                            NP
      GOTO 25
   24 RMCTU1=CTU1(1)**2+STU1(7)*CTU1(1)*CTU1(2)+STU1(13)*CTU1(1)*CTU1(3)NP
      RMDTU1=CTU1(2)**2+STU1(7)*CTU1(1)*CTU1(2)+STU1(13)*CTU1(1)*CTU1(3)NP
     1+CTU1(3)**2                                                        NP
      RMCTU2=CTU1(7)**2+STU1(7)*CTU1(7)*CTU1(8)+STU1(13)*CTU1(7)*CTU1(9)NP
      RMDTU2=CTU1(8)**2+STU1(7)*CTU1(7)*CTU1(8)+STU1(13)*CTU1(7)*CTU1(9)NP
     1+CTU1(9)**2                                                        NP
      RMCTU3=CTU1(13)**2+STU1(7)*CTU1(13)*CTU1(14)+STU1(13)*CTU1(13)     NP
     1*CTU1(15)                                                          NP
      RMDTU3=CTU1(14)**2+CTU1(15)**2+STU1(7)*CTU1(13)*CTU1(14)           NP
     1+STU1(13)*CTU1(13)*CTU1(15)                                        NP
      GA2=6.*RMCTU2+6.*RMCTU3                                            NP
   25 WRITE OUTPUT TAPE 6,1000
 1000 FORMAT(1H1)
      WRITE OUTPUT TAPE 6,1001,TITLE
 1001 FORMAT(12A6/12A6)
      WRITE OUTPUT TAPE 6,1002,JOB
 1002 FORMAT(1H0,14H TRIAL NUMBER I3)
```

```
      WRITE OUTPUT TAPE 6,1003,AL1,BE1,GA1
 1003 FORMAT(1HO  7H ALPHA F10.6,6H BETA F10.6,7H GAMMA F10.6)
      WRITE OUTPUT TAPE 6,1004,((HA(I,J),I=1,M),J=1,M)
 1004 FORMAT(1HO 8H H(A1G) 6F11.6)
      WRITE OUTPUT TAPE 6,1005,((HE(I,J),I=1,M),J=1,M)
 1005 FORMAT(1H 8H H(EG)  6F11.6)
      WRITE OUTPUT TAPE 6,1006,((HTG(I,J),I=1,M),J=1,M)
 1006 FORMAT(1H  8H H(T2G) 6F11.6)
      WRITE OUTPUT TAPE 6,1007,((HTU(I,J),I=1,M),J=1,M)
 1007 FORMAT(1H  8H H(T1U) 6F11.6)
      WRITE OUTPUT TAPE6,1021,(HTU1(13),HTU1(15))                          NP
 1021 FORMAT(1H F41.6,F11.6)                                               NP
      WRITE OUTPUT TAPE 6,1008,((SA(I,J),I=1,M),J=1,M)
 1008 FORMAT(1HO 8H S(A1G) 6F11.6)
      WRITE OUTPUT TAPE 6,1009,((SE(I,J),I=1,M),J=1,M)
 1009 FORMAT(1H 8H S(EG)  6F11.6)
      WRITE OUTPUT TAPE 6,1010,((STG(I,J),I=1,M),J=1,M)
 1010 FORMAT(1H  8H S(T2G) 6F11.6)
      WRITE OUTPUT TAPE 6,1011,((STU(I,J),I=1,M),J=1,M)
 1011 FORMAT(1H 8H S(T1U) 6F11.6)
      WRITE OUTPUT TAPE6,1022,(STU1(3),STU1(13),STU1(15))                  NP
 1022 FORMAT(1H F30.6,2F11.6)                                              NP
      WRITE OUTPUT TAPE 6,1012,(EA(1),CA1(1),CA1(2),RMCA1,RMDA1,RSCA1,
     1RSDA1)
 1012 FORMAT(1HO9H A(1G) E F11.6,6H EVEC 2F10.6,9H POP NOS 4F10.6)
      WRITE OUTPUT TAPE 6,1013,(ETU(1),CTU1(1),CTU1(2),RMCTU1,RMDTU1,
     1RSCTU1,RSDTU1)
 1013 FORMAT(1HO9H T(1U) E F11.6,6H EVEC 2F10.6,9H POP NOS 4F10.6)
      WRITE OUTPUT TAPE 6,1023,(CTU1(3))                                   NP
 1023 FORMAT(F46.6)                                                        NP
      WRITE OUTPUT TAPE 6,1014,(EE(1),CE1(1),CE1(2),RMCE1,RMDE1,RSCE1,
     1RSDE1)
 1014 FORMAT(1HO8H E(G) E F12.6,6H EVEC 2F10.6,9H POP NOS 4F10.6)
      WRITE OUTPUT TAPE 6,1015,( ETG(1),CTG1(1) ,CTG1(2),RMCTG1,RMDTG1,
     1RSCTG1,RSDTG1)
 1015 FORMAT(1HO9H T(2G) E F11.6,6H EVEC 2F10.6,9H POP NOS 4F10.6)
```

```
      WRITE OUTPUT TAPE 6,1016,(ETU(3),CTU1(13),CTU1(14),RMCTU3,RMDTU3, NP
     1RSCTU3,RSDTU3)                                                    NP
 1016 FORMAT(1H09H T(1U) E F11.6,6H EVEC 2F10.6,9H POP NOS 4F10.6)       NP
      WRITE OUTPUT TAPE 6,1023,(CTU1(15))                               NP
      WRITE OUTPUT TAPE6,1015,(ETG(2),CTG1(7),CTG1(8),RMCTG2,
     1RMDTG2,RSCTG2,RSDTG2)
      WRITE OUTPUT TAPE6,1013,(ETU(2),CTU1(7),CTU1(8),RMCTU2,RMDTU2,
     1RSCTU2,RSDTU2)
      WRITE OUTPUT TAPE 6,1023,(CTU1(9))                                NP
      WRITE OUTPUT TAPE 6,1017,(EE(2),CE1(7),CE1(8),RMCE2,RMDE2,RSCE2,
     1RSDE2)
 1017 FORMAT(1H09H  E(G) E F11.6,6H EVEC 2F10.6,9H POP NOS 4F10.6)
      WRITE OUTPUT TAPE 6,1018,(EA(2),CA1(7),CA1(8),RMCA2,RMDA2,RSCA2,
     1RSDA2)
 1018 FORMAT(1H09H A(1G) E F11.6,6H EVEC 2F10.6,9H POP NOS 4F10.6)
      WRITE OUTPUT TAPE 6,1019,(AL2,BE2,GA2)
 1019 FORMAT(1H014H OUTPUT ALPHA F10.6,6H BETA F10.6,7H GAMMA F10.6)
      ETOT=2.*EA(2)+4.*EE(2)+6.*(ETU(2)+ETG(2)+ETU(3))+(9.-ZZ-P)*ETG(1) M NP
     1+P*EE(1)                                                          NP
      WRITE OUTPUT TAPE 6,1050,ETOT
 1050 FORMAT(1HO 16H TOTAL ENERGY =  F15.6)
      CALL ADJAL  (AL1,AL2,N)
      CALL ADJBE  (BE1,BE2,N1)
      CALL ADJGA  (GA1,GA2,N2)
      IF(N) 26,26,1
   26 IF(N1)27,27,1
   27 IF(N2)29,29,1
   29 WRITE OUTPUT TAPE 6,1020
 1020 FORMAT(17H SELF CONSISTANT )
   33 READ INPUT TAPE 5,901,MORE
      IF(MORE)30,30,31
   30 CALL EXIT
      END
```

```
      SUBROUTINE DIAG(H,S,E,C)
      DIMENSION H(6,6),S(6,6),E(6),C(6,6),X(6),V(6,6),D(6,6),
     1VDL(6,6),G(6,6),GG(6,6),B(6,6),VD(6,6)
      COMMON M
      DO 1 J=1,M
      DO 1 I=1,M
      H(J,I)=H(I,J)
    1 S(J,I)=S(I,J)
      CALL VALVEC (S,X,V)
      DO 12 I=1,M
   12 D(I,I)=1.0/SQRTF(X(I))
      DO 2 I=1,M
      DO 2 J=1,M
      VD(I,J)=0.0
      DO 3 K=1,M
    3 VD(I,J)=VD(I,J)+(V(I,K)*D(K,J))
    2 CONTINUE
      DO  4 I=1,M
      DO 4 J=1,M
      VDL(I,J)=0.0
      DO 5 K=1,M
    5 VDL(I,J)=VDL(I,J)+(VD(I,K)*V(J,K))
    4 CONTINUE
      DO 6 I=1,M
      DO 6 J=1,M
      G(I,J)=0.0
      DO 7 K=1,M
    7 G(I,J)=G(I,J)+(VDL(I,K)*H(K,J))
    6 CONTINUE
      DO 8 I=1,M
      DO 8 J=1,M
      GG(I,J)=0.0
      DO 9 K=1,M
    9 GG(I,J)=GG(I,J)+(G(I,K)*VDL(K,J))
    8 CONTINUE
      CALL VALVEC (GG,E,B)
```

```
      DO 10 I=1,M
      DO 10 J=1,M
      C(I,J)=0.0
      DO 11 K=1,M
11    C(I,J)=C(I,J)+(VOL(I,K)*B(K,J))
10    CONTINUE
      RETURN
      END
```

```
      SUBROUTINE VALVEC(A,EVAL,VECTOR)
      DIMENSION A(6,6),EVAL(6),VECTOR(6,6),ARRAY(400),VECT(400)
      COMMONM
      K=0
       DO 10 I=1,M
      DO 10 J=1,M
      K=K+1
   10 ARRAY(K)=A(I,J)
      CALL JACFUL(M,ARRAY,VECT,ITER,TRACE)
       L=1
      DO 20 L1=1,M
      EVAL(L1)=ARRAY(L)
   20 L=L+M+1
      K1=0
      DO 30 I1=1,M
      DO 30 J1=1,M
      K1=1+K1
   30 VECTOR(J1,I1)=VECT(K1)
      RETURN
      END
```

```
      SUBROUTINE ADJAL  (DEL1,DEL2,N)
      DIMENSION DEL(99),DELD(99)
      COMMON M,KAL,KBE,KGA
      KAL=KAL+1
      N=0
      DEL(KAL)=DEL1
      DELD(KAL)=ABSF(DEL1-DEL2)
      IF(DELD(KAL)-.001) 10,10,1
    1 IF(KAL-1) 2,2,3
    2 DEL1=(DEL1+DEL2)/2.
      GO TO 9
    3 IF(DELD(KAL)-DELD(KAL-1)) 2,4,4
    4 DEL1=(DEL(KAL-1)+DEL(KAL))/2.
    9 N=1
   10 RETURN
      END
      SUBROUTINE ADJBE  (DEL1,DEL2,N)
      DIMENSION DEL(99),DELD(99)
      COMMON M,KAL,KBE,KGA
      KBE=KBE+1
      N=0
      DEL(KBE)=DEL1
      DELD(KBE)=ABSF(DEL1-DEL2)
      IF(DELD(KBE)-.001) 10,10,1
    1 IF(KBE-1) 2,2,3
    2 DEL1=(DEL1+DEL2)/2.
      GO TO 9
    3 IF(DELD(KBE)-DELD(KBE-1)) 2,4,4
    4 DEL1=(DEL(KBE-1)+DEL(KBE))/2.
    9 N=1
   10 RETURN
      END
      SUBROUTINE ADJGA  (DEL1,DEL2,N)
      DIMENSION DEL(99),DELD(99)
      COMMON M,KAL,KBE,KGA
      KGA=KGA+1
```

```
      N=0
      DEL(KGA)=DEL1
      DELD(KGA)=ABSF(DEL1-DEL2)
      IF(DELD(KGA)-.001) 10,10,1
    1 IF(KGA-1) 2,2,3
    2 DEL1=(DEL1+DEL2)/2.
      GO TO 9
    3 IF(DELD(KGA)-DELD(KGA-1)) 2,4,4
    4 DEL1=(DEL(KGA-1)+DEL(KGA))/2.
    9 N=1
   10 RETURN
      END
```

APPENDIX IV

The following is the format that has been used for the tables of this appendix.

Name of complex Wavefunction of metal atom Experimental 10Dq (cm^{-1})

No pi : Pi bonding has been omitted

or pi : Pi bonding has been included

Method of estimating the resonance integral

Smith-population analysis	Mulliken-population analysis
Self-consistent populations of metal d, s and p orbitals. Self-consistent charge on the metal atom. Calculated 10Dq (cm^{-1}) Calculated total energy (kK) (kK = kiloKaiser = 10^3 cm^{-1})	Same as for Smith.

a: This method does not lead to convergence.

b: The energy of the pi symmetry orbital on the donor atom is above the energy of the d orbital on the metal atom and the energy levels have been scrambled.

c: Same as b but the energy levels have not been scrambled.

TABLE 9

SELF-CONSISTENT PARAMETERS FOR $[Fe(H_2O)_6]^{2+}$

$[Fe(H_2O)_6]^{2+}$	Fe^{1+}	10,400 cm^{-1}	$[Fe(H_2O)_6]^{2+}$	Fe^{1+}	10,400 cm^{-1}
No pi			No pi		
Ballhausen and Gray			Wolfsberg and Helmholz		
Smith	Mulliken		Smith	Mulliken	
	$d^{6.265}$ $s^{0.431}$ $p^{0.319}$		$d^{6.670}$ $s^{0.349}$ $p^{0.898}$	$d^{6.190}$ $s^{0.447}$ $p^{0.662}$	
a	0.985 28,208 cm^{-1} -4,628 kK		0.083 17,973 cm^{-1} -4,234 kK	0.701 26,172 cm^{-1} -4,622 kK	
$[Fe(H_2O)_6]^{2+}$	Fe^{1+}	10,400 cm^{-1}	$[Fe(H_2O)_6]^{2+}$	Fe^{1+}	10,400 cm^{-1}
pi			pi		
Ballhausen and Gray			Wolfsberg and Helmholz		
Smith	Mulliken		Smith	Mulliken	
	$d^{6.587}$ $s^{0.344}$ $p^{0.203}$		$d^{6.684}$ $s^{0.358}$ $p^{0.918}$	$d^{6.327}$ $s^{0.411}$ $p^{0.663}$	
a	0.866 16,039 cm^{-1} -6,263 kK		0.040 16,059 cm^{-1} -6,390 kK	0.599 19,603 cm^{-1} -6,429 kK	

TABLE 9 - Continued

$[Fe(H_2O)_6]^{2+}$	Fe^{2+}	10,400 cm^{-1}	$[Fe(H_2O)_6]^{2+}$	Fe^{2+}	10,400 cm^{-1}
No pi			No pi		
Ballhausen and Gray			Wolfsberg and Helmholz		
Smith	Mulliken		Smith	Mulliken	
	$d^{6.200}$ $s^{0.449}$ $p^{0.341}$		$d^{6.637}$ $s^{0.351}$ $p^{0.921}$	$d^{6.138}$ $s^{0.461}$ $p^{0.656}$	
a	1.010 17,102 cm^{-1} -4,695 kK		0.091 10,037 cm^{-1} -4,275 kK	0.745 15,497 cm^{-1} -4,689 kK	

$[Fe(H_2O)_6]^{2+}$	Fe^{2+}	10,400 cm^{-1}	$[Fe(H_2O)_6]^{2+}$	Fe^{2+}	10,400 cm^{-1}
pi			pi		
Ballhausen and Gray			Wolfsberg and Helmholz		
Smith	Mulliken		Smith	Mulliken	
	d 6.542 s 0.359 p 0.208		d 6.644 s 0.360 p 0.939	d 6.275 s 0.427 p 0.648	
a	0.891 8,580 cm^{-1} -6,282 kK		0.057 9,038 cm^{-1} -6,411 kK	0.650 11,119 cm^{-1} -6,449 kK	

TABLE 9 - Continued

$[Fe(H_2O)_6]^{2+}$	Fe^{3+}	10,400 cm^{-1}
No pi		
Ballhausen and Gray		
Smith		Mulliken
$d^{6.611}$ $s^{0.300}$ $p^{1.084}$		$d^{6.148}$ $s^{0.470}$ $p^{0.330}$
0.005 3,269 cm^{-1} -4,300 kK		1.052 10,325 cm^{-1} -4,746 kK

$[Fe(H_2O)_6]^{2+}$	Fe^{3+}	10,400 cm^{-1}
No pi		
Wolfsberg and Helmholz		
Smith		Mulliken
$d^{6.619}$ $s^{0.352}$ $p^{0.932}$		$d^{6.100}$ $s^{0.480}$ $p^{0.601}$
0.097 5,523 cm^{-1} -4,297 kK		0.819 9,218 cm^{-1} -4,741 kK

$[Fe(H_2O)_6]^{2+}$	Fe^{3+}	10,400 cm^{-1}
pi		
Ballhausen and Gray		
Smith		Mulliken
$d^{6.614}$ $s^{0.300}$ $p^{1.070}$		
0.016 2,958 cm^{-1} -6,462 kK		b

$[Fe(H_2O)_6]^{2+}$	Fe^{3+}	10,400 cm^{-1}
pi		
Wolfsberg and Helmholz		
Smith		Mulliken
$d^{6.622}$ $s^{0.362}$ $p^{0.947}$		$d^{6.262}$ $s^{0.442}$ $p^{0.581}$
0.069 5,005 cm^{-1} -6,421 kK		0.715 5,987 cm^{-1} -6,446 kK

TABLE 10

SELF-CONSISTENT PARAMETERS FOR $[Fe(H_2O)_6]^{3+}$

$[Fe(H_2O)_6]^{3+}$	Fe^{1+}	13,700 cm^{-1}	$[Fe(H_2O)_6]^{3+}$	Fe^{1+}	13,700 cm^{-1}
No pi			No pi		
Ballhausen and Gray			Wolfsberg and Helmholz		
Smith		Mulliken	Smith		Mulliken
$d^{5.830}$ $s^{0.416}$ $p^{0.924}$		$d^{5.543}$ $s^{0.556}$ $p^{0.656}$	$d^{5.824}$ $s^{0.447}$ $p^{0.995}$		$d^{5.454}$ $s^{0.564}$ $p^{0.929}$
0.830 36,017 cm^{-1} -4,859 kK		1.245 53,883 cm^{-1} -5,083 kK	0.734 37,554 cm^{-1} -4,900 kK		1.053 50,088 cm^{-1} -5,128 kK
$[Fe(H_2O)_6]^{3+}$	Fe^{1+}	13,700 cm^{-1}	$[Fe(H_2O)_6]^{3+}$	Fe^{1+}	13,700 cm^{-1}
pi			pi		
Ballhausen and Gray			Wolfsberg and Helmholz		
Smith		Mulliken	Smith		Mulliken
$d^{6.002}$ $s^{0.378}$ $p^{0.997}$			$d^{5.983}$ $s^{0.425}$ $p^{1.024}$		$d^{5.918}$ $s^{0.471}$ $p^{0.807}$
0.623 23,601 cm^{-1} -6,958 kK		b	0.568 28,044 cm^{-1} -7,036 kK		0.804 28,363 cm^{-1} -7,028 kK

TABLE 10 - Continued

$[Fe(H_2O)_6]^{3+}$	Fe^{2+}	13,700 cm^{-1}	$[Fe(H_2O)_6]^{3+}$	Fe^{2+}	13,700 cm^{-1}
No pi			No pi		
Ballhausen and Gray			Wolfsberg and Helmholz		
Smith		Mulliken	Smith		Mulliken
$d^{5.771}$ $s^{0.425}$ $p^{0.940}$		$d^{5.478}$ $s^{0.570}$ $p^{0.688}$	$d^{5.759}$ $s^{0.452}$ $p^{1.045}$		$d^{5.388}$ $s^{0.577}$ $p^{0.952}$
0.864 22,187 cm^{-1} -4,932 kK		1.264 35,336 cm^{-1} -5,164 kK	0.744 22,496 cm^{-1} -4,970 kK		1.083 32,309 cm^{-1} -5,212 kK
$[Fe(H_2O)_6]^{3+}$	Fe^{2+}	13,700 cm^{-1}	$[Fe(H_2O)_6]^{3+}$	Fe^{2+}	13,700 cm^{-1}
pi			pi		
Ballhausen and Gray			Wolfsberg and Helmholz		
Smith		Mulliken	Smith		Mulliken
$d^{5.942}$ $s^{0.389}$ $p^{0.984}$			$d^{5.894}$ $s^{0.432}$ $p^{1.070}$		
0.685 14,276 cm^{-1} -6,973 kK		b	0.604 16,710 cm^{-1} -7, 066 kK		b

TABLE 10 - Continued

$[Fe(H_2O)_6]^{3+}$	Fe^{3+}	13,700 cm^{-1}	$[Fe(H_2O)_6]^{3+}$	Fe^{3+}	13,700 cm^{-1}
No pi			No pi		
Ballhausen and Gray			Wolfsberg and Helmholz		
Smith		Mulliken	Smith		Mulliken
$d^{5.726}$ $s^{0.431}$ $p^{0.955}$		$d^{5.431}$ $s^{0.588}$ $p^{0.665}$	$d^{5.713}$ $s^{0.455}$ $p^{1.072}$		$d^{5.343}$ $s^{0.596}$ $p^{0.907}$
0.888 13,278 cm^{-1} -4,979 kK		1.316 23,568 cm^{-1} -5,222 kK	0.760 13,210 cm^{-1} -5,010 kK		1.154 21,297 cm^{-1} -5,271 kK
$[Fe(H_2O)_6]^{3+}$	Fe^{3+}	13,700 cm^{-1}	$[Fe(H_2O)_6]^{3+}$	Fe^{3+}	13,700 cm^{-1}
pi			pi		
Ballhausen and Gray			Wolfsberg and Helmholz		
Smith		Mulliken	Smith		Mulliken
$d^{5.891}$ $s^{0.399}$ $p^{0.980}$			$d^{5.828}$ $s^{0.438}$ $p^{1.094}$		
0.730 8,337 cm^{-1} -6,983 kK		b	0.640 9,732 cm^{-1} -7,078 kK		b

TABLE 11

SELF-CONSISTENT PARAMETERS FOR $[Co(H_2O)_6]^{2+}$

$[Co(H_2O)_6]^{2+}$	Co^o	9,700 cm^{-1}					
No pi							
Ballhausen and Gray							
Smith		Mulliken					
	$d^{7.386}$	$s^{0.463}$	$p^{0.164}$				
a	0.987 48,422 cm^{-1} -5,530 kK						

$[Co(H_2O)_6]^{2+}$	Co^o	9,700 cm^{-1}					
No pi							
Wolfsberg and Helmholz							
Smith				Mulliken			
	$d^{7.749}$	$s^{0.369}$	$p^{0.920}$	$d^{7.321}$	$s^{0.488}$	$p^{0.414}$	
a	-0.038 30,281 cm^{-1} -5,320 kK			0.777 46,839 cm^{-1} -5,576 kK			

$[Co(H_2O)_6]^{2+}$	Co^o	9,700 cm^{-1}					
pi							
Ballhausen and Gray							
Smith		Mulliken					
	$d^{7.613}$	$s^{0.380}$	$p^{0.164}$				
a	0.843 26,868 cm^{-1} -6,457 kK						

$[Co(H_2O)_6]^{2+}$	Co^o	9,700 cm^{-1}					
pi							
Wolfsberg and Helmholz							
Smith				Mulliken			
	$d^{7.768}$	$s^{0.367}$	$p^{0.932}$	$d^{7.454}$	$s^{0.445}$	$p^{0.459}$	
a	-0.067 26,869 cm^{-1} -6,476 kK			0.642 32,506 cm^{-1} -6,567 kK			

TABLE 11 - Continued

$[Co(H_2O)_6]^{2+}$	Co^{1+}	9,700 cm^{-1}	$[Co(H_2O)_6]^{2+}$	Co^{1+}	9,700 cm^{-1}
No pi			No pi		
Ballhausen and Gray			Wolfsberg and Helmholz		
Smith	Mulliken		Smith	Mulliken	
	$d^{7.287}$ $s^{0.463}$ $p^{0.315}$		$d^{7.695}$ $s^{0.374}$ $p^{0.929}$	$d^{7.201}$ $s^{0.473}$ $p^{0.683}$	
a	0.935 29,268 cm^{-1} -5,583 kK		0.002 17,713 cm^{-1} -5,367 kK	0.643 26,627 cm^{-1} -5,634 kK	

$[Co(H_2O)_6]^{2+}$	Co^{1+}	9,700 cm^{-1}	$[Co(H_2O)_6]^{2+}$	Co^{1+}	9,700 cm^{-1}
pi			pi		
Ballhausen and Gray			Wolfsberg and Helmholz		
Smith	Mulliken		Smith	Mulliken	
	$d^{7.542}$ $s^{0.390}$ $p^{0.231}$		$d^{7.704}$ $s^{0.371}$ $p^{0.951}$	$d^{7.294}$ $s^{0.444}$ $p^{0.705}$	
a	0.837 14,752 cm^{-1} -6,506 kK		-0.026 15,797 cm^{-1} -6,524 kK	0.557 19,302 cm^{-1} -6,661 kK	

TABLE 11 - Continued

$[Co(H_2O)_6]^{2+}$	Co^{2+}	9,700 cm^{-1}	$[Co(H_2O)_6]^{2+}$	Co^{2+}	9,700 cm^{-1}
No pi			No pi		
Ballhausen and Gray			Wolfsberg and Helmholz		
Smith	Mulliken		Smith	Mulliken	
	$d^{7.222}$ $s^{0.480}$ $p^{0.342}$		$d^{7.663}$ $s^{0.376}$ $p^{0.952}$	$d^{7.148}$ $s^{0.486}$ $p^{0.684}$	
a	0.956 18,142 cm^{-1} -5,619 kK		0.009 10,101 cm^{-1} -5,389 kK	0.682 16,114 cm^{-1} -5,668 kK	
$[Co(H_2O)_6]^{2+}$	Co^{2+}	9,700 cm^{-1}	$[Co(H_2O)_6]^{2+}$	Co^{2+}	9,700 cm^{-1}
pi			pi		
Ballhausen and Gray			Wolfsberg and Helmholz		
Smith	Mulliken		Smith	Mulliken	
	$d^{7.515}$ $s^{0.400}$ $p^{0.227}$		$d^{7.667}$ $s^{0.374}$ $p^{0.972}$	$d^{7.250}$ $s^{0.457}$ $p^{0.690}$	
a	0.858 7,171 cm^{-1} -6,525 kK		-0.013 9,072 cm^{-1} -6,548 kK	0.603 10,957 cm^{-1} -6,686 kK	

TABLE 12

SELF-CONSISTENT PARAMETERS FOR $[Co(H_2O)_6]^{3+}$

$[Co(H_2O)_6]^{3+}$ Co^{1+} 19,100 cm^{-1} No pi Ballhausen and Gray		$[Co(H_2O)_6]^{3+}$ Co^{1+} 19,100 cm^{-1} No pi Wolfsberg and Helmholz	
Smith	Mulliken	Smith	Mulliken
$d^{6.893}$ $s^{0.426}$ $p^{0.975}$	$d^{6.870}$ $s^{0.529}$ $p^{0.488}$	$d^{6.892}$ $s^{0.460}$ $p^{1.018}$	$d^{6.721}$ $s^{0.548}$ $p^{0.852}$
0.706 35,697 cm^{-1} -6,060 kK	1.113 48,232 cm^{-1} -6,136 kK	0.630 37,882 cm^{-1} -6,132 kK	0.879 45,724 cm^{-1} -6,238 kK
$[Co(H_2O)_6]^{3+}$ Co^{1+} 19,100 cm^{-1} pi Ballhausen and Gray		$[Co(H_2O)_6]^{3+}$ Co^{1+} 19,100 cm^{-1} pi Wolfsberg and Helmholz	
Smith	Mulliken	Smith	Mulliken
$d^{6.880}$ $s^{0.419}$ $p^{1.048}$	$d^{6.824}$ $s^{0.519}$ $p^{0.606}$	$d^{6.882}$ $s^{0.456}$ $p^{1.082}$	$d^{6.685}$ $s^{0.541}$ $p^{0.946}$
0.653 25,138 cm^{-1} -7,268 kK	1.051 55,398 cm^{-1} -7,293 kK	0.580 29,035 cm^{-1} -7,352 kK	0.828 58,822 cm^{-1} -7,427 kK

TABLE 12 - Continued

$[Co(H_2O)_6]^{3+}$	Co^{2+}	19,100 cm^{-1}	$[Co(H_2O)_6]^{3+}$	Co^{2+}	19,100 cm^{-1}
No pi			No pi		
Ballhausen and Gray			Wolfsberg and Helmholz		
Smith		Mulliken	Smith		Mulliken
$d^{6.852}$ $s^{0.433}$ $p^{0.978}$		$d^{6.765}$ $s^{0.550}$ $p^{0.552}$	$d^{6.838}$ $s^{0.463}$ $p^{1.068}$		$d^{6.617}$ $s^{0.566}$ $p^{0.898}$
0.737 22,241 cm^{-1} -6,062 kK		1.133 32,161 cm^{-1} -6,158 kK	0.631 22,999 cm^{-1} -6,134 kK		0.919 29,939 cm^{-1} -6,260 kK
$[Co(H_2O)_6]^{3+}$	Co^{2+}	19,100 cm^{-1}	$[Co(H_2O)_6]^{3+}$	Co^{2+}	19,100 cm^{-1}
pi			pi		
Ballhausen and Gray			Wolfsberg and Helmholz		
Smith		Mulliken	Smith		Mulliken
$d^{6.837}$ $s^{0.427}$ $p^{1.046}$			$d^{6.827}$ $s^{0.459}$ $p^{1.126}$		$d^{6.587}$ $s^{0.561}$ $p^{0.974}$
0.690 14,878 cm^{-1} -7,273 kK		b	0.588 17,494 cm^{-1} -7,361 kK		0.878 6,944 cm^{-1} (c) -7,447 kK

TABLE 12 - Continued

$[Co(H_2O)_6]^{3+}$	Co^{3+}	19,100 cm^{-1}	$[Co(H_2O)_6]^{3+}$	Co^{3+}	19,100 cm^{-1}
No pi			No pi		
Ballhausen and Gray			Wolfsberg and Helmholz		
Smith		Mulliken	Smith		Mulliken
$d^{6.808}$ $s^{0.440}$ $p^{0.988}$		$d^{6.682}$ $s^{0.573}$ $p^{0.562}$	$d^{6.790}$ $s^{0.467}$ $p^{1.099}$		$d^{6.547}$ $s^{0.587}$ $p^{0.871}$
0.764 13,756 cm^{-1} -6,068 kK		1.183 21,831 cm^{-1} -6,174 kK	0.644 13,927 cm^{-1} -6,134 kK		0.995 20,098 cm^{-1} -6,271 kK
$[Co(H_2O)_6]^{3+}$	Co^{3+}	19,100 cm^{-1}	$[Co(H_2O)_6]^{3+}$	Co^{3+}	19,100 cm^{-1}
pi			pi		
Ballhausen and Gray			Wolfsberg and Helmholz		
Smith		Mulliken	Smith		Mulliken
$d^{6.796}$ $s^{0.435}$ $p^{1.046}$			$d^{6.781}$ $s^{0.463}$ $p^{1.151}$		$d^{6.520}$ $s^{0.582}$ $p^{0.940}$
0.723 8,359 cm^{-1} -7,277 kK		b	0.605 10,386 cm^{-1} -7,361 kK		0.958 22,546 cm^{-1} -7,449 kK

TABLE 13

SELF-CONSISTENT PARAMETERS FOR $[Ni(H_2O)_6]^{2+}$

$[Ni(H_2O)_6]^{2+}$	Ni^0	8,500 cm^{-1}	$[Ni(H_2O)_6]^{2+}$	Ni^0	8,500 cm^{-1}
No pi			No pi		
Ballhausen and Gray			Wolfsberg and Helmholz		
Smith	Mulliken		Smith	Mulliken	
	$d^{8.407}$ $s^{0.351}$ $p^{0.211}$		$d^{8.724}$ $s^{0.395}$ $p^{0.918}$	$d^{8.333}$ $s^{0.365}$ $p^{0.478}$	
a	1.031 42,433 cm^{-1} -5,077 kK		-0.037 24,474 cm^{-1} -4,437 kK	0.824 40,147 cm^{-1} -5,062 kK	

$[Ni(H_2O)_6]^{2+}$	Ni^0	8,500 cm^{-1}	$[Ni(H_2O)_6]^{2+}$	Ni^0	8,500 cm^{-1}
pi			pi		
Ballhausen and Gray			Wolfsberg and Helmholz		
Smith	Mulliken		Smith	Mulliken	
	$d^{8.370}$ $s^{0.334}$ $p^{0.344}$		$d^{8.732}$ $s^{0.392}$ $p^{0.933}$	$d^{8.305}$ $s^{0.353}$ $p^{0.588}$	
a	0.952 11,576 cm^{-1} (c) -5,153 kK		-0.057 21,831 cm^{-1} -4,827 kK	0.754 21,556 cm^{-1} (c) -5,157 kK	

TABLE 13 - Continued

$[Ni(H_2O)_6]^{2+}$	Ni^{1+}	8,500 cm^{-1}	$[Ni(H_2O)_6]^{2+}$	Ni^{1+}	8,500 cm^{-1}
No pi			No pi		
Ballhausen and Gray			Wolfsberg and Helmholz		
Smith	Mulliken		Smith	Mulliken	
	$d^{8.300}$ $s^{0.352}$ $p^{0.374}$		$d^{8.679}$ $s^{0.399}$ $p^{0.933}$	$d^{8.207}$ $s^{0.353}$ $p^{0.738}$	
a	0.974 25,117 cm^{-1} -5,159 kK		-0.011 13,788 cm^{-1} -4,514 kK	0.702 22,371 cm^{-1} -5,126 kK	

$[Ni(H_2O)_6]^{2+}$	Ni^{1+}	8,500 cm^{-1}	$[Ni(H_2O)_6]^{2+}$	Ni^{1+}	8,500 cm^{-1}
pi			pi		
Ballhausen and Gray			Wolfsberg and Helmholz		
Smith	Mulliken		Smith	Mulliken	
			$d^{8.681}$ $s^{0.397}$ $p^{0.955}$	$d^{8.194}$ $s^{0.344}$ $p^{0.807}$	
a	b		-0.033 12,341 cm^{-1} -4,872 kK	0.655 11,796 cm^{-1} -5,197 kK	

TABLE 13 - Continued

$[Ni(H_2O)_6]^{2+}$	Ni^{2+}	8,500 cm^{-1}	$[Ni(H_2O)_6]^{2+}$	Ni^{2+}	8,500 cm^{-1}	
No pi			No pi			
Ballhausen and Gray			Wolfsberg and Helmholz			
Smith	Mulliken		Smith		Mulliken	
	$d^{8.239}$ $s^{0.371}$ $p^{0.388}$		$d^{8.654}$ $s^{0.401}$ $p^{0.956}$		$d^{8.160}$ $s^{0.370}$ $p^{0.718}$	
a	1.002 15,914 cm^{-1} -5,230 kK		-0.011 7,847 cm^{-1} -4,543 kK		0.752 13,838 cm^{-1} -5,200 kK	
$[Ni(H_2O)_6]^{2+}$	Ni^{2+}	8,500 cm^{-1}	$[Ni(H_2O)_6]^{2+}$	Ni^{2+}	8,500 cm^{-1}	
pi			pi			
Ballhausen and Gray			Wolfsberg and Helmholz			
Smith	Mulliken		Smith		Mulliken	
			$d^{8.655}$ $s^{0.399}$ $p^{0.975}$		$d^{8.149}$ $s^{0.362}$ $p^{0.774}$	
a	b		-0.029 7,060 cm^{-1} -4,893 kK		0.715 1,525 cm^{-1} (c) -5,237 kK	

TABLE 14

SELF-CONSISTENT PARAMETERS FOR $[Co(NH_3)_6]^{2+}$ AND $[Co(NH_3)_6]^{3+}$

$[Co(NH_3)_6]^{2+}$	Co^{1+}	10,500 cm^{-1}	$[Co(NH_3)_6]^{2+}$	Co^{1+}	10,500 cm^{-1}
No pi			No pi		
Ballhausen and Gray			Wolfsberg and Helmholz		
Smith	Mulliken		Smith	Mulliken	
	$d^{7.415}$ $s^{0.576}$ $p^{0.400}$		$d^{7.856}$ $s^{0.448}$ $p^{1.160}$	$d^{7.296}$ $s^{0.573}$ $p^{0.758}$	
a	0.609 32,674 cm^{-1} -3,681 kK		-0.464 15,304 cm^{-1} -3,106 kK	0.373 28,980 cm^{-1} -3,664 kK	
$[Co(NH_3)_6]^{2+}$	Co^{2+}	10,500 cm^{-1}	$[Co(NH_3)_6]^{2+}$	Co^{2+}	10,500 cm^{-1}
No pi			No pi		
Ballhausen and Gray			Wolfsberg and Helmholz		
Smith	Mulliken		Smith	Mulliken	
	$d^{7.346}$ $s^{0.590}$ $p^{0.449}$		$d^{7.821}$ $s^{0.451}$ $p^{1.164}$	$d^{7.232}$ $s^{0.585}$ $p^{0.796}$	
a	0.615 21,380 cm^{-1} -3,717 kK		-0.436 9,131 cm^{-1} -3,137 kK	0.387 18,396 cm^{-1} -3,702 kK	

TABLE 14 - Continued

$[Co(NH_3)_6]^{3+}$	Co^{2+}	23,500 cm^{-1}	$[Co(NH_3)_6]^{3+}$	Co^{2+}	23,500 cm^{-1}
No pi			No pi		
Ballhausen and Gray			Wolfsberg and Helmholz		
Smith		Mulliken	Smith		Mulliken
$d^{6.970}$ $s^{0.526}$ $p^{1.258}$		$d^{6.990}$ $s^{0.635}$ $p^{0.630}$	$d^{6.977}$ $s^{0.559}$ $p^{1.263}$		$d^{6.812}$ $s^{0.644}$ $p^{0.981}$
0.246 19,977 cm^{-1} -3,809 kK		0.745 34,048 cm^{-1} -4,043 kK	0.201 21,646 cm^{-1} -3,846 kK		0.563 31,368 cm^{-1} -4,081 kK
$[Co(NH_3)_6]^{3+}$	Co^{3+}	23,500 cm^{-1}	$[Co(NH_3)_6]^{3+}$	Co^{3+}	23,500 cm^{-1}
No pi			No pi		
Ballhausen and Gray			Wolfsberg and Helmholz		
Smith		Mulliken	Smith		Mulliken
$d^{6.945}$ $s^{0.541}$ $p^{1.236}$		$d^{6.920}$ $s^{0.653}$ $p^{0.652}$	$d^{6.939}$ $s^{0.569}$ $p^{1.290}$		$d^{6.750}$ $s^{0.662}$ $p^{0.978}$
0.278 12,904 cm^{-1} -3,821 kK		0.775 24,126 cm^{-1} -4,062 kK	0.202 13,546 cm^{-1} -3,846 kK		0.610 22,065 cm^{-1} -4,105 kK

TABLE 15

SELF-CONSISTENT PARAMETERS FOR $[Ni(NH_3)_6]^{2+}$

$[Ni(NH_3)_6]^{2+}$	Ni^{1+}	10,800 cm^{-1}	$[Ni(NH_3)_6]^{2+}$	Ni^{1+}	10,800 cm^{-1}
	No pi			No pi	
	Ballhausen and Gray			Wolfsberg and Helmholz	
Smith	Mulliken		Smith	Mulliken	
	$d^{8.322}$ $s^{0.552}$ $p^{0.722}$		$d^{8.860}$ $s^{0.454}$ $p^{1.186}$	$d^{8.275}$ $s^{0.577}$ $p^{0.868}$	
a	0.404 26,423 cm^{-1} -3,865 kK		-0.500 13,261 cm^{-1} -3,175 kK	0.280 25,546 cm^{-1} -3,856 kK	

$[Ni(NH_3)_6]^{2+}$	Ni^{2+}	10,800 cm^{-1}	$[Ni(NH_3)_6]^{2+}$	Ni^{2+}	10,800 cm^{-1}
	No pi			No pi	
	Ballhausen and Gray			Wolfsberg and Helmholz	
Smith	Mulliken		Smith	Mulliken	
	$d^{8.265}$ $s^{0.569}$ $p^{0.744}$		$d^{8.830}$ $s^{0.457}$ $p^{1.188}$	$d^{8.219}$ $s^{0.590}$ $p^{0.878}$	
a	0.422 17,377 cm^{-1} -3,906 kK		-0.475 8,011 cm^{-1} -3,207 kK	0.313 16,511 cm^{-1} -3,899 kK	

TABLE 16

SELF-CONSISTENT PARAMETERS FOR $[Co(H_2O)_6]^{2+}$ AND $[Co(H_2O)_6]^{3+}$ IN THEIR FIRST EXCITED STATE

$[Co(H_2O)_6]^{2+}$	Co^{2+}	9,700 cm^{-1}		$[Co(H_2O)_6]^{3+}$	Co^{2+}	19,100 cm^{-1}	
No pi				No pi			
Wolfsberg and Helmholz				Wolfsberg and Helmholz			
Smith		Mulliken		Smith		Mulliken	
$d^{7.668}$	$s^{0.375}$ $p^{0.952}$	$d^{7.082}$	$s^{0.495}$ $p^{0.710}$	$d^{6.819}$	$s^{0.465}$ $p^{1.070}$	$d^{6.527}$	$s^{0.582}$ $p^{0.937}$
0.005 10,070 cm^{-1} -5,376 kK		0.713 16,796 cm^{-1} -5,679 kK		0.746 23,363 cm^{-1} -6,119 kK		0.954 13,834 cm^{-1} -6,269 kK	
$[Co(H_2O)_6]^{2+}$	Co^{2+}	9,700 cm^{-1}		$[Co(H_2O)_6]^{3+}$	Co^{2+}	19,100 cm^{-1}	
pi				pi			
Wolfsberg and Helmholz				Wolfsberg and Helmholz			
Smith		Mulliken		Smith		Mulliken	
$d^{7.676}$	$s^{0.373}$ $p^{0.971}$	$d^{7.279}$	$s^{0.452}$ $p^{0.678}$	$d^{6.873}$	$s^{0.454}$ $p^{1.117}$	$d^{6.778}$	$s^{0.527}$ $p^{0.890}$
-0.020 9,030 cm^{-1} -6,536 kK		0.591 11,055 cm^{-1} -6,665 kK		0.556 17,446 cm^{-1} -7,330 kK		0.805 14,192 cm^{-1} -7,365 kK	

TABLE 17

SELF-CONSISTENT PARAMETERS FOR $[Co(H_2O)_6]^{3+}$ AND $[Co(H_2O)_6]^{3+}$ AT 1.93 A^o USING THE AFTERNANT PROCEDURE FOR THE DONOR ATOM COULOMB INTEGRAL

$[Co(H_2O)_6]^{3+}$	Co^{3+}	19,100 cm^{-1}	$[Co(H_2O)_6]^{3+}$	Co^{3+}	19,100 cm^{-1}
No pi			No pi		
Ballhausen and Gray			Wolfsberg and Helmholz		
Smith		Mulliken	Smith		Mulliken
$d^{6.811}$ $s^{0.441}$ $p^{0.988}$		$d^{6.685}$ $s^{0.574}$ $p^{0.564}$	$d^{6.792}$ $s^{0.467}$ $p^{1.100}$		$d^{6.550}$ $s^{0.589}$ $p^{0.872}$
0.760 13,764 cm^{-1} -4,845 kK		1.177 21,873 cm^{-1} -5,030 kK	0.641 13,929 cm^{-1} -4,887 kK		0.989 20,097 cm^{-1} -5,091 kK
$[Co(H_2O)_6]^{3+}$	Co^{3+}	19,100 cm^{-1}	$[Co(H_2O)_6]^{3+}$	Co^{3+}	19,100 cm^{-1}
pi			pi		
Ballhausen and Gray			Wolfsberg and Helmholz		
Smith		Mulliken	Smith		Mulliken
$d^{6.799}$ $s^{0.436}$ $p^{1.047}$			$d^{6.784}$ $s^{0.464}$ $p^{1.151}$		
0.718 8,213 cm^{-1} -7,239 kK		b	0.601 10,301 cm^{-1} -7,321 kK		b

TABLE 17 - Continued

$[Co(H_2O)_6]^{3+}$ at 1.93 A° Co^{3+} 19,100 cm^{-1} No pi Ballhausen and Gray	
Smith	Mulliken
$d^{6.829}$ $s^{0.439}$ $p^{1.009}$	$d^{6.706}$ $s^{0.575}$ $p^{0.567}$
0.723 15,835 cm^{-1} -4,832 kK	1.152 24,817 cm^{-1} -5,023 kK

$[Co(H_2O)_6]^{3+}$ at 1.93 A° Co^{3+} 19,100 cm^{-1} No pi Wolfsberg and Helmholz	
Smith	Mulliken
$d^{6.814}$ $s^{0.467}$ $p^{1.111}$	$d^{6.565}$ $s^{0.589}$ $p^{0.892}$
0.608 16,252 cm^{-1} -4,878 kK	0.954 22,879 cm^{-1} -5,086 kK

$[Co(H_2O)_6]^{3+}$ at 1.93 A° Co^{3+} 19,100 cm^{-1} pi Ballhausen and Gray	
Smith	Mulliken
$d^{6.911}$ $s^{0.418}$ $p^{1.063}$	
0.608 10,446 cm^{-1} -7,215 kK	b

$[Co(H_2O)_6]^{3+}$ at 1.93 A° Co^{3+} 19,100 cm^{-1} pi Wolfsberg and Helmholz	
Smith	Mulliken
$d^{6.866}$ $s^{0.457}$ $p^{1.154}$	
0.523 12,239 cm^{-1} -7,303 kK	b

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BIOGRAPHICAL SKETCH

William Adkins Feiler, Jr. was born October 9, 1940, in Paducah, Kentucky. After attending elementary and junior high public schools in Paducah, Kentucky, he was graduated from Paducah Tilghman High School in June, 1958. In June, 1962, he received the degree of Bachelor of Science in Chemical Engineering from the University of Kentucky, Lexington, Kentucky.

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This dissertation was prepared under the direction of the chairman of the candidate's supervisory committee and has been approved by all members of that committee. It was submitted to the Dean of the College of Arts and Sciences and to the Graduate Council, and was approved as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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